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CHARACTERIZATION OF AND TREATMENT

RECOMMENDATIONS FOR THE ST. LOUIS

ADIT DRAINAGE AND ASSOCIATED

SETTLING PONDS IN

RICO, COLORADO

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering).

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# ABSTRACT

The current treatment method for treating the drainage from the St. Louis adit near Rico, Colorado involves lime neutralization and gravity sedimentation of the resulting precipitates in a series of ponds prior to discharge into the Dolores River. The purpose of this study was to evaluate the effectiveness of this conventional treatment process, examine the long-term fate of metals in the drainage and ponds, and propose alternative treatment technologies. Results from this study indicate a 40% loss of water throughout the pond system due to possible seeps and ground water infiltration, and only marginal success regarding the removal of the CPDES permitted metals (Cd, Cu, Pb, Ag, and Zn). Both zinc and cadmium exceed the 30-day average permit limitations of 0.237 mg/L and 0.0004 mg/L, respectively. An analysis of the water and sediment in the ponds indicates that 98% of the suspended solids in the treated drainage settles in the upper ponds closest to the mine, and that the settled solids are primarily iron and calcium. Furthermore, the upper ponds are at 75% of their capacity due to the buildup of sediment resulting in channelized flow. This has caused a 74% reduction in the residence time in the upper ponds needed to facilitate sedimentation, and a spillover of solids into the lower ponds. To bring the CPDES permitted metals back into compliance, dredging of the upper ponds has been recommended as a short-term extension to the lifetime of the current treatment process while alternative remediation technologies are evaluated. Proposed alternatives include lime neutralization with sludge recycle, biogenic $H_2S$ sulfide precipitation using municipal sewage sludge as an electron donor, and constructed wetlands.

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Chapter 1

INTRODUCTION

The problems faced by mining and mineral processing companies pertaining to mine drainage, soils and groundwater contamination, and water treatment has become a serious environmental concern. Drainage associated with metal mines usually contains elevated concentrations of metals which can pose dangers to downstream human and aquatic communities. The most common method employed to treat mine drainage is chemical neutralization and precipitation using lime. While sometimes effective, this conventional pump-and-treat method is often costly and inefficient. In addition to producing large volumes of unstable metal hydroxide sludges which may be labeled hazardous and therefore expensive to dispose of, the long term commitment associated with treating drainage which could persist over hundreds of years is daunting. As a result of the short-comings of the lime treatment process and the increasing trend towards more stringent, government-imposed discharge guidelines, identification and ultimate application of cost-effective and efficient methods for cleaning up metal-bearing waters has become a priority.

The Chemical Engineering Department at the Colorado School of Mines (CSM) first became involved in mine drainage remediation in January, 1995, as a member of an alternative remediation technology team directed by Dr. Travis L. Hudson of the Atlantic Richfield Company (ARCO). Dr. Hudson, Remediation Technology and Support Manager, assembled this group with the purpose of identifying existing or developing remediation technologies that could have current or future impact on ARCO's remediation of former Anaconda properties. The program was a collaborative effort on behalf of

ARCO Corporate Environmental Remediation-Denver, CSM, and ARCO Exploration and Production Technology.

The Colorado School of Mines' contribution to the program included technical support for purposes of identification and engineering evaluation of alternate water treatment processes that may be applicable to ARCO's mining and mineral processing sites. These preliminary investigations provided the impetus for the evolution of this thesis; the evaluation of the St. Louis adit[1] discharge, located in the Rico-Argentine mining area in Rico, Colorado.

The work performed on this project was conducted in conjunction with a thorough site characterization of the town of Rico and the surrounding Rico-Argentine mining area, executed by ARCO within the framework of the Colorado Voluntary Cleanup and Redevelopment Act. This voluntary strategy is a proactive approach that invites all relevant and affected parties to develop a remedial plan that is satisfactory and equitable to all involved. It is hoped that this strategy will help prevent costly regulatory and legal actions. Although considered a part of the Rico-Argentine mining area, the St. Louis adit discharge is regulated by the Colorado Department of Health through a Colorado Pollution Discharge Elimination System (CPDES) permit, which disqualifies it from the voluntary cleanup act. However, the essence of the voluntary concept has been applied to this site as well.

## 1.1 Research Objectives

The current treatment method, employed for the past twelve years to treat the drainage from the St. Louis adit, involves lime addition and settling of the resulting precipitates in a series of sedimentation ponds. This method has been only partially

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[1] Adit is a term often used to describe a horizontal entrance to a mine.

effective, and over the years, it has become exceedingly more difficult to meet permit requirements. In addition, it has become very evident that this is not a long-term solution for this site. The ponds are at or near capacity after only twelve years of operation, and there is no indication that the adit flow will be diminishing any time in the near future. Hence, it is the intent of this research project to evaluate alternative treatment methods pertinent to the St. Louis adit drainage. To achieve this goal, the following objectives were established:

1. Collect pertinent historical data relating flow rates and liming rates providing the tools necessary to formulate an estimate of the lifetime of the ponds, and a correlation between residence time and pond efficiency.

2. Summarize current and previous work performed at the site. This should include a critique of the current water treatment plant, and a survey of other processes evaluated for the treatment of the St. Louis adit drainage.

3. Characterize the site by performing field and laboratory analysis of the drainage and associated settling ponds.

4. Investigate the application of software available for process modeling of complex systems using standard chemical engineering processes.

5. Provide recommendations for further study.

## 1.2 Site Description

The St. Louis adit and associated settling ponds are located on the eastern edge of Dolores County approximately 1/2 mile north of the town of Rico, Colorado, as illustrated in Figure 1.1. The entire site skirts the eastern bank of the Dolores river and occupies about 80 acres. Rico, at an altitude of 8800 feet, is surrounded by the 12,000 foot peaks of the Rico Mountains in the San Juan National Forest. Twenty five miles to the northeast is the town of Telluride, and 44 miles to the southwest is the town of Cortez.

The water emanating from the St. Louis adit originates in mine workings aggregating several miles. This discharge is treated with quick-lime (CaO) and is regulated by CPDES permit No. CO-0029793, through the Colorado Department of Health. It is understood that the flow from the adit represents generalized groundwater seepage and storm water run-off. According to weather observations received from the National Weather Service from 1961 to 1995, the mean annual precipitation and snowfall measured at the Rico Climatological Station (Station NO. 05-7017-2), are 29.46 and 181.92 inches, respectively.

The ponds are contained within man-made dikes constructed in unconsolidated material underlain by an alluvial aquifer and a major geothermal fault. This geothermal fault zone appears to be the source of artesian flows which naturally flow into the river via numerous hot springs located along the rivers banks (Weir et al. 1983; Pratt et al. 1969; Cross et al. 1905). This phenomena is evidenced by the occurrence of bubbles of carbon dioxide and geothermal wells throughout the lower series of treatment ponds. According to reports from the Colorado Department of Health, the ponds were constructed with native material without liners or run-on/run-off controls (Schrack 1995).

The configuration of the site in 1980 consisted of 19 settling ponds, a heap leach pad and sulfuric acid plant north of the ponds, and maintenance buildings north and east of the ponds (Figure 1.2).
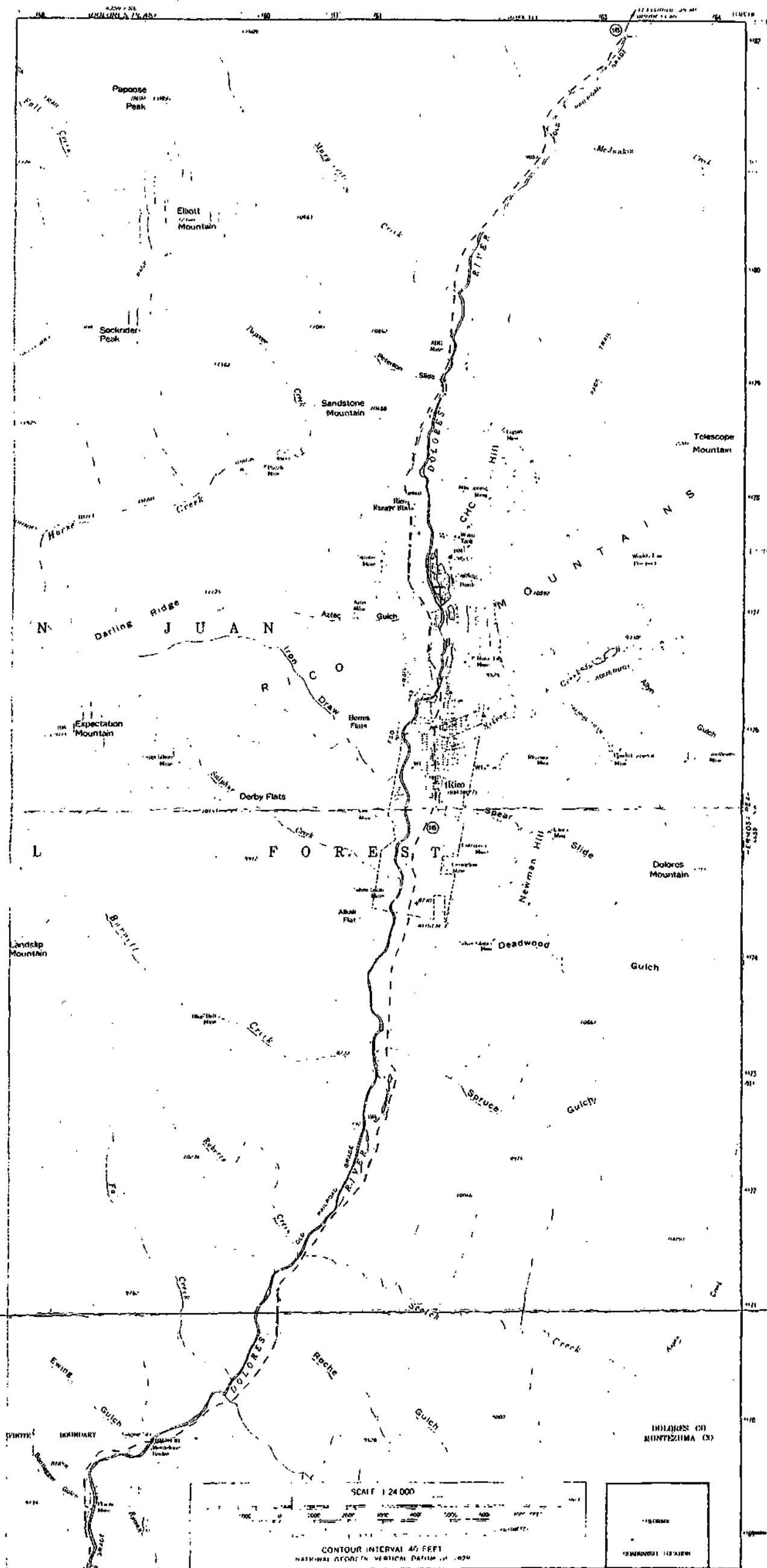
Figure 1.1.  Site location map with the St. Louis adit settling ponds just north of Rico.
Source:  USGS Rico, Colorado 7.5 minute Quadrangle.

# Color Map(s)

## The following pages contain color that does not appear in the scanned images.

To view the actual images, please contact the Superfund Records Center at (303) 312-6473.
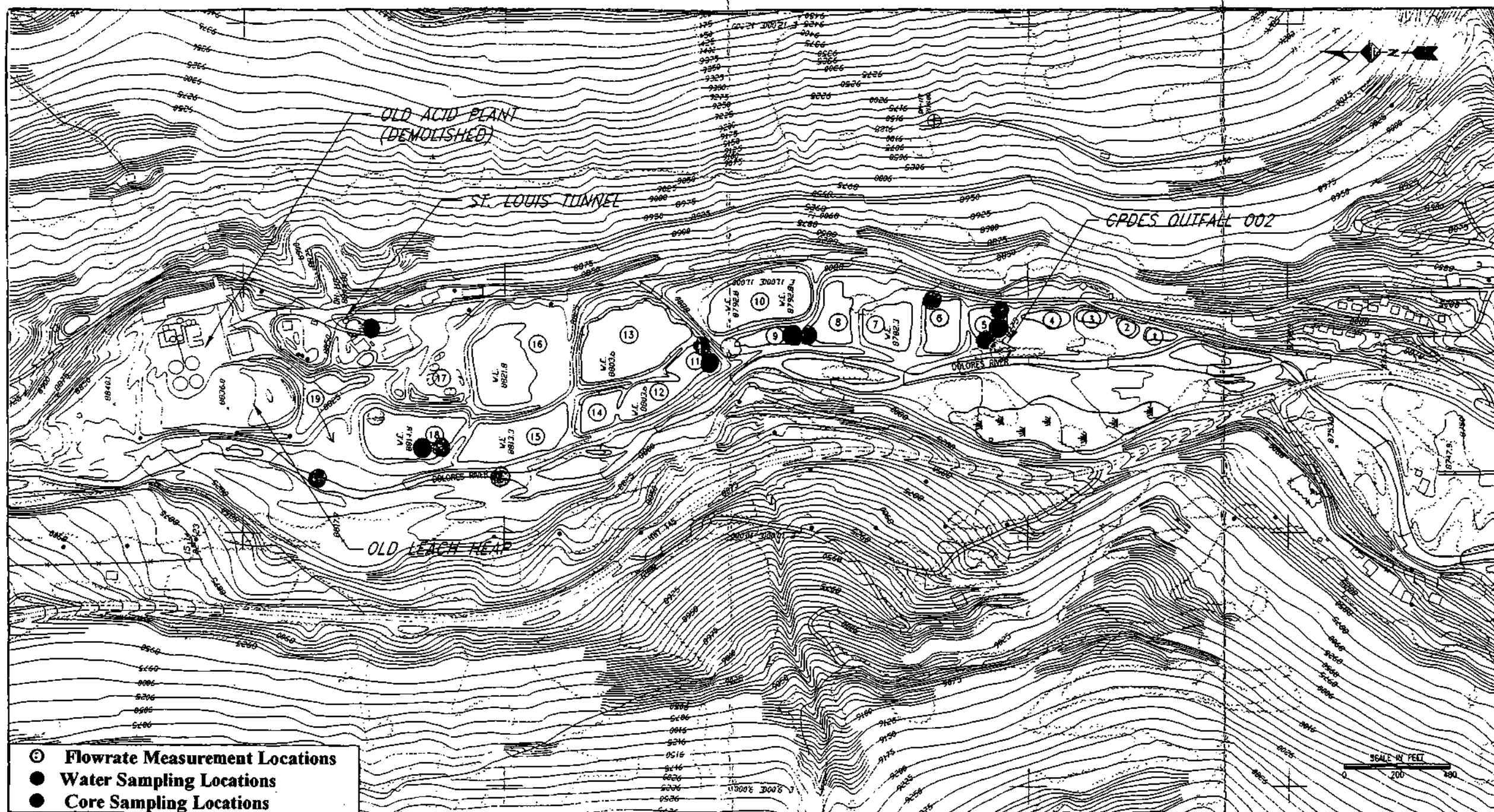
Figure 1.2. St. Louis settling ponds in Rico, Colorado with approximate sampling locations.
Source: Atlantic Richfield Company, 1980.

However, to date, the acid plant and maintenance buildings have been demolished, and the heap leach pad has been remediated. Only 10 of the 19 ponds are currently being used for water treatment. Ponds 16, 17, and 19 have been completely back-filled. Pond 13 is completely drained of water, but not back-filled. There is a strong suggestion of calcine tailings from the old acid production plant evidenced by dark, brick-red sediment. Pond 10 is full of water, however there is no visible connection to the rest of the system. Ponds 1 through 4 have been allowed to become a natural wetland and exhibit an abundance of plant and wildlife. The previous heap leach pad site is now a new pond, with a volume of approximately 625,000 cubic feet. It is currently being used as a holding area for dredged material (Figure 1.3). CPDES Outfall 002 currently exits to the Dolores River at Pond 5. In addition, a lime treatment plant has been installed at the St. Louis adit, and has been treating the mine drainage since 1984. Figure 1.4 shows the location of the treatment plant in relation to the adit and the first settling pond (pond 18).

# Color Photo(s)

## The following pages contain color that does not appear in the scanned images.

To view the actual images, please contact the Superfund Records Center at (303) 312-6473.

Figure 1.3. New holding pond estimated to be approximately 625,000 cubic feet. The St. Louis adit drainage is located to the east, just outside the right hand side of the photo.

Figure 1.4. Location of the water treatment plant in relation to the adit and the first settling pond. The adit is located directly behind the plant, and the pond in the foreground is pond 18.

## 1.3 Organization

The purpose of this thesis is to identify existing or developing technologies that could have an impact on the remediation of the St. Louis adit drainage and associated settling ponds. To meet this objective, it is necessary to have an understanding of the nature of mine drainage and available remediation technologies. Most importantly, the specific characteristic of a site and any regulatory constraints must be determined before practical recommendations can be made.

The organization of this thesis provides the reader with a comprehensive guide to the problem and resulting recommendations for the remediation of this site. The introduction outlines the motivation for this research and presents the location and description of the area. Chapter 2, the literature survey, provides the background necessary to understand the nature of the problem and the proposed solutions. It includes the history of the site, a description of the chemistry of mine drainage, and the technical aspects of pertinent remediation technologies. Chapter 3 describes the experimental methods and equipment used to characterize the site. Chapter 4 provides a detailed discussion of the results and the treatment options proposed. Chapters 5 and 6 outline the conclusions of this research and the resulting recommendations, with suggestions for future work.

Chapter 2

LITERATURE SURVEY

## 2.1 Introduction

Mine drainage is a critical problem throughout the United States. Thousands of miles of creeks and rivers are effected. many located in Colorado. Polluted sites, a reminder of Colorado's mining past, dot the map from the Denver area to the Western slope. The environmental impact of these mines range from unfavorable esthetics to metals and sediment transport and acidic drainage. Hence. it is essential to know how mine drainage conditions are generated. and how they can be mitigated.

The process of mine drainage treatment begins with an understanding of the source and effect of water pollutants. A characterization is then developed and interpreted to forecast treatment needs. In addition, site specific characteristics and the features of existing and proposed treatment systems must be considered. This knowledge will help provide insights into the appropriate remediation techniques which could be applied at a specific site. This chapter is intended to provide background information on the Rico site, an introduction to the origin of mine drainage, and a general understanding of the possible treatment options available.

## 2.2 Site History

The Rico-Argentine mining site began operations over 100 years ago as a silver producer. The major goals of the now inactive mining operations consisted of precious metal mining, base metal production (lead, zinc, and copper) from sulfide ores, and sulfuric acid production from pyrite ores. The St. Louis adit drainage and associated settling ponds on the Dolores River are considered an extension of this mining area, and are the focus of this study.

A series of ponds have been used for the last 12 years to assist in the remediation of mine drainage from the St. Louis adit. However, historical data provided by ARCO indicates that the ponds have been in existence since the 1950's and have been used for other purposes as well. The following is a chronological summary of significant background information pertaining to previous operational and remedial activities in the Rico-Argentine mining area, prepared for ARCO by ESA Consultants Inc. of Fort Collins, Colorado (ESA 1995).

1869   The first mining claim was established along the Dolores River in Rico

1872   The first crude smelter was built. It produced three bars of bullion before collapsing.

1880   The Grand View Mining & Smelting Company built a small smelting operation on the east bank of the Dolores River near the bridge just North of the town of Rico. This was motivated by high freight cost to ship the ore to Durango   ($300/ton)

1883   A temporary peak in silver production occurred producing 193,360 ounces of silver.

1884   A second smelter was built at the southern end of town, and operated for two years.

1887   The famous Enterprise gold-silver blanket ore body was discovered in the
       Enterprise Mine shaft. This shaft was located in the Newman Hill area southeast
       of the town.

1893   An all-time peak in production in silver and gold occurred. 2,675,000 ounces of
       silver, and 442,000 ounces of gold were recovered. At this time, the population of
       Rico grew to 12,000 and 20 active mines producing gold, silver, lead, zinc, and
       copper were in operation. However, in mid 1893 a silver panic gripped the area
       and a decline in silver production was experienced.

1902   Intermittent mining activity began and lasted until 1925. The principal production
       was base-metal ores such as lead and zinc. The ore was shipped to custom
       flotation mills in the Salt Lake City area. During this time, the Rico-Argentine
       mining company incorporated, and a temporary peak for base metals was
       experienced, producing 1,540 tons lead, 1,300 tons zinc, and 916 tons copper.
       Most of the copper was mined primarily from the Mountain Spring-Wellington
       mine of the Rico-Wellington Mining Company in CHC Hill.

1925   The St. Louis Smelting & Refining Company, a division of the National Lead
       Company and after May 1927 the successor of the Rico Mining and Reduction
       Company, mined the CHC Hill, the Silver Swan Mine, and along the Silver Creek
       (Figure 1.1). Other chief producing companies during this time included the Rico-
       Argentine Mining Company, Union Carbonate Mines, Inc., and the International
       Smelting Company (a subsidiary of Anaconda).

1926   The International Smelting Company operated the Falcon Mill located at the North
       end of town between highway 145 and the Dolores River until 1928. After the
       mill shut down, the ore was once again shipped to custom mills in the Salt Lake
       City area.

1927   An all-time peak in base metals was experienced. 4,994 tons of lead, 5,308 tons of
       zinc, and 65 tons of copper were mined.

1929  Rico, along with the rest of America, was hit by the Great Depression. By 1932, all production ceased. However, mining resumed on a small scale in 1934. During this time. the St. Louis Smelting and Refining Company drove the St. Louis Tunnel and crosscut extensions into the east bank of the Dolores River under CHC Hill. This caused the tunnel to become a continuous source of mine water discharge into the Dolores River.

1939  The Rico-Argentine Mining Company began operation of the lead-zinc-copper Argentine Mine along with the Argentine Mill. The mill was a 150 ton per day flotation mill located on the Silver Creek.

1941  The Falcon Mill which ceased operations in 1928 was dismantled.

1955  A crosscut from the Argentine Mine on the Silver Creek to the St. Louis Tunnel on the Dolores river was complete. This caused the water level in the Silver Creek area workings to drop 450 feet, reducing the impact of drainage at this site but increasing the flow rate from the St. Louis adit. In addition, the Rico-Argentine Mining Company began operation of the Dolores River acid plant. The plant was located at the St. Louis Tunnel, and processed 165 tons per day of iron pyrite ore producing 0.3 million tons of sulfuric acid to supply uranium mills. This operation generated calcine (iron oxide) tailings which were deposited in what is now considered ponds 11 through 18, see Figure 2.1 (Stephens 1978).

1964  The acid plant was closed by the state for polluting the Dolores River. Fumes from the plant destroyed the vegetation along the valley and adjacent hillsides.

1971  The Rico-Argentine Mining Company mining operations ceased, and the lower 500 feet of tunnels were allowed to flood discharging to the Dolores River at the St. Louis adit.

1973  The Rico-Argentine Mining Company began operation of a 100,000 ton heap leach pad adjacent to the acid plant to extract gold and silver from dump material from the Newman Hill area.

1975    A cyanide heap leach berm failure occurred resulting in an extensive fish kill in the Dolores River. This caused an immediate closure of the site.

1976    The first Colorado Pollution Discharge Elimination System (CPDES) permit. No. CO-0029793, was issued to the Rico-Argentine Mining Company for the St. Louis adit discharge into the Dolores River.

1977    The Rico-Argentine Mining Company merged with the Crystal Oil Company.

1978    The Crystal Oil Company hired Hazen Research, Inc. to sample the calcine tailings in the ponds. The result of their research indicated the ponds contained 234.230 tons of tailings that were suitable for use as an iron additive in the cement industry.

1980    The Anaconda Copper Company acquired the Rico-Argentine Mining Company from the Crystal Oil Company, and the discharge permit was transfered to Anaconda. Anaconda began conducting a deep exploration drilling program for molybdenum ore bodies and performed numerous reclamation and stabilization procedures of the site until 1983.

1983    The State of Colorado filed a Natural Resources Damage claim pursuant to CERCLA (the Comprehensive Environmental Response. Compensation, and Liability Act). However, the EPA denied the claim and the discharge permit was renewed.

1984    Anaconda began operation of a lime addition plant with a series of settling ponds to treat the drainage from the St. Louis adit.

1986    Anaconda, noting poor treatment efficiencies obtained by the old treatment system, added a new lime-slaking facility. In addition, Anaconda removed hazardous substances from the Rico facility and demolished the acid plant and associated structures. The site was then regraded, capped with a soil cover, and revegitated.

1988    ARCO, who briefly owned this site, sold the real estate, mining and commercial properties to Rico Development Inc.
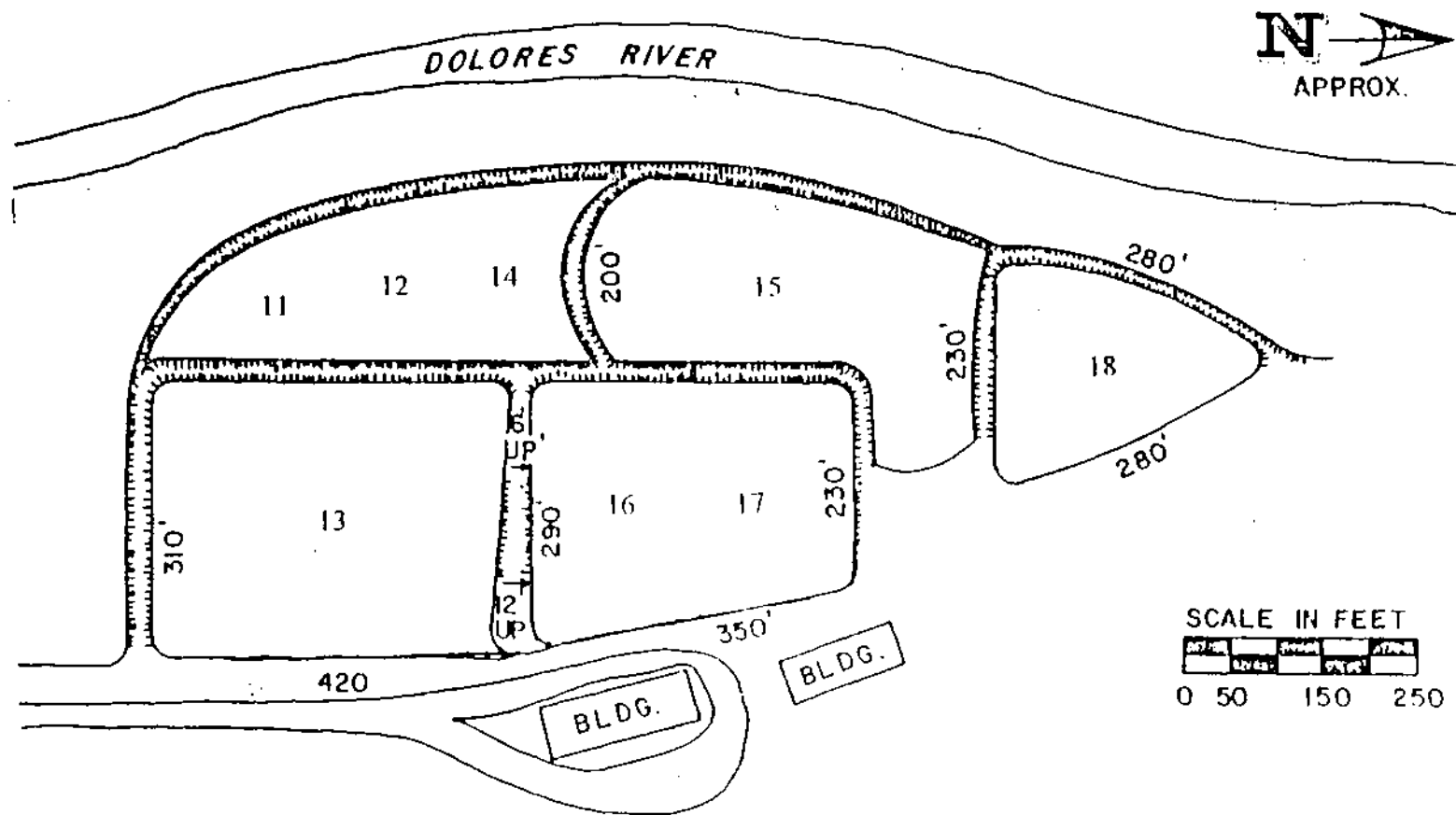
Figure 2.1. Sketch of the Rico-Argentine tailings ponds as they were configured from 1955 to 1978. The ponds were used during this time to hold calcine tailings from the Dolores River acid plant.
Source: Stephens 1978.

Since Rico Development Inc. acquired the holdings. the heap leach pad site was remediated and replaced with a stabilization basin of approximately 625,000 cubic feet, and is currently being used to hold dredged tailings from the upper most ponds. In addition. the water treatment plant continues to operate adding..on average. 600 lbs/day of quicklime (CaO).

## 2.2.1 Current Water Treatment Plant

Rico Development, Inc. currently operates and maintains a mine water treatment facility for the removal of heavy metals from the mine discharge prior to its permitted discharge into the Dolores River. This heavy metals removal process incorporates neutralization and settling technology, and consists of raising the pH of the water by the addition of quicklime and settling the resulting flocculant in a series of ponds. Studies conducted by the Colorado School of Mines Research Institute (CSMRI) in 1982. indicated that zinc and copper concentrations in the St. Louis adit waters could be removed from solution with lime precipitation at a pH above 8.7 to concentrations below permit limitations. In addition, laboratory work found that adding approximately 30 mg/L of hydrated lime ($Ca(OH)_2$) would raise the pH of the drainage to the necessary value (CSMRI 1982). This estimate was based on an average annual flow rate of 2000 gallons per minute (gpm) and translates to approximately 600 lbs/day of quicklime (CaO). Since the adit flow rate displays seasonal variations, the treatment process was designed to accommodate varied liming rates.

The lime slaking plant[2] consists of a water pumping system, lime storage, slaking reactor, slurry storage, and a discharge system. All the components of this system are

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[2] The slaking plant was manufactured by Smith & Loveless, Inc., located in Lenexa, Kansas.

contained within a pre-manufactured Chem-Tower building supplied by Smith & Loveless (Smith & Loveless 1986). Figure 2.2 is an illustration of the treatment plant provided by the manufacturer.

Water to the treatment plant flows from the mine through a cement channel emanating from the St. Louis adit. The water flows to a concrete access box located northeast of the building. This box contains an intake line which feeds the slaker via a pump. Only a small amount of the total flow from the mine passes through the water treatment plant. The remaining water is diverted through an underground PVC pipe to a ditch which flows into pond 18. The water that is pumped to the treatment plant is fed directly to a reactor where it is mixed with quicklime to produce a calcium hydroxide slurry.

The quicklime is stored in the upper part of the tower, which has a capacity of 1,240 cubic feet (250.000 lbs CaO). Based on an average liming rate of 600 lbs/day, this equates to a roughly estimated 12 month supply of lime. The dry lime is fed through a bin activator, a collar which shakes the bottom of the bin to ensure the lime will flow freely. Lime next enters the volumetric screw feeder, where a controller allows for adjustment of the screw speed and thus the rate of lime feeding. A totalizer shows the actual hours of operation of the feeder. Thus, the total lime used in a 24 hour period may be determined. The lime then drops through a slide gate into the reactor. The lime feed system starts and stops automatically by level controls associated with the lime slurry holding tank. Upon demand, the slide gate begins to open. When the gate is fully open, the reactor, feeder, and bin activator are on.

The reactor is a baffled container with a turbine agitator at the bottom for stirring. The maximum lime feed rate to the reactor is 500 lbs/hr and provides a mixture retention time of 10 minutes. Water and lime are vigorously mixed in the reactor, producing an exothermic reaction which converts pebble quicklime to calcium hydroxide. Vigorous mixing enhances the reaction process by stripping hydrated lime particles from the surface

of the pebble quicklime. The lime slurry exits the reactor chamber by flowing under a baffle and over a weir into the classifier chamber.

The classifier is a wedged-shaped box with an inclined screw, which when rotating serves to separate the grit from the slurry. A high impact weir jet is directed onto the slurry as it overflows the weir to break it up into a finely divided milk of lime solution. The heavier grit particles settle to the bottom where the screw lifts the grit to a discharge opening located at the upper end of a grit conveyor trough. At the base of the classifier, dilution water is added via turbulence jets. This serves to maintain the calcium hydroxide particles in suspension for carry over into the slurry storage chamber, cleanse the grit of calcium hydroxide particles, and minimize the opportunity for the slurry to plug the plumbing. Slurry spills from the classifier into a slurry storage tank on the ground floor of the plant, where electrodes are used to indicate the level in the tank. The slurry is agitated by a turbine mixer to keep the lime particles and any remaining grit in suspension.

Lime discharge is controlled by a motorized ball valve located at the bottom of the slurry tank. This valve is the key to the control of lime usage. The valve is controlled by timers that can be set to open at any time of day for a specified number of seconds. Thus, the lime is discharged into the remaining water evenly throughout the day with minimal supervision.

The limed water enters a series of 10 ponds designed to provide a residence time of approximately nine days. During this time, the effect of gravity on the particles suspended in the water induces sedimentation. Solids are removed throughout the system, until the water reaches a discharge flume at pond 5. Here, the water flows through a calibrated flume and then into the Dolores River. The object of the entire system is to discharge water that meets the CPDES permit limitations.

8' 0"

4 " SCH 40 FILL PIPE

$\frac{3}{16}$

LOW LEVEL BIN
SWITCH

11' 0"

12'-0" Dia.

LIME STORAGE

$\frac{1}{4}$"

BIN ACTIVATOR

MAINTENANCE GATE

$\frac{1}{4}$"

FLEXIBLE CONNECTION

VARIABLE RATE
FEEDER

15' 0"

MOTORIZED SLIDE GATE
ON SLAKER INLET

CLASSIFIER

SLAKING REACTOR

SLURRY STORAGE TANK
WITH MIXER

8' 4"

Insulation

7⅞

SUMP     DRAIN
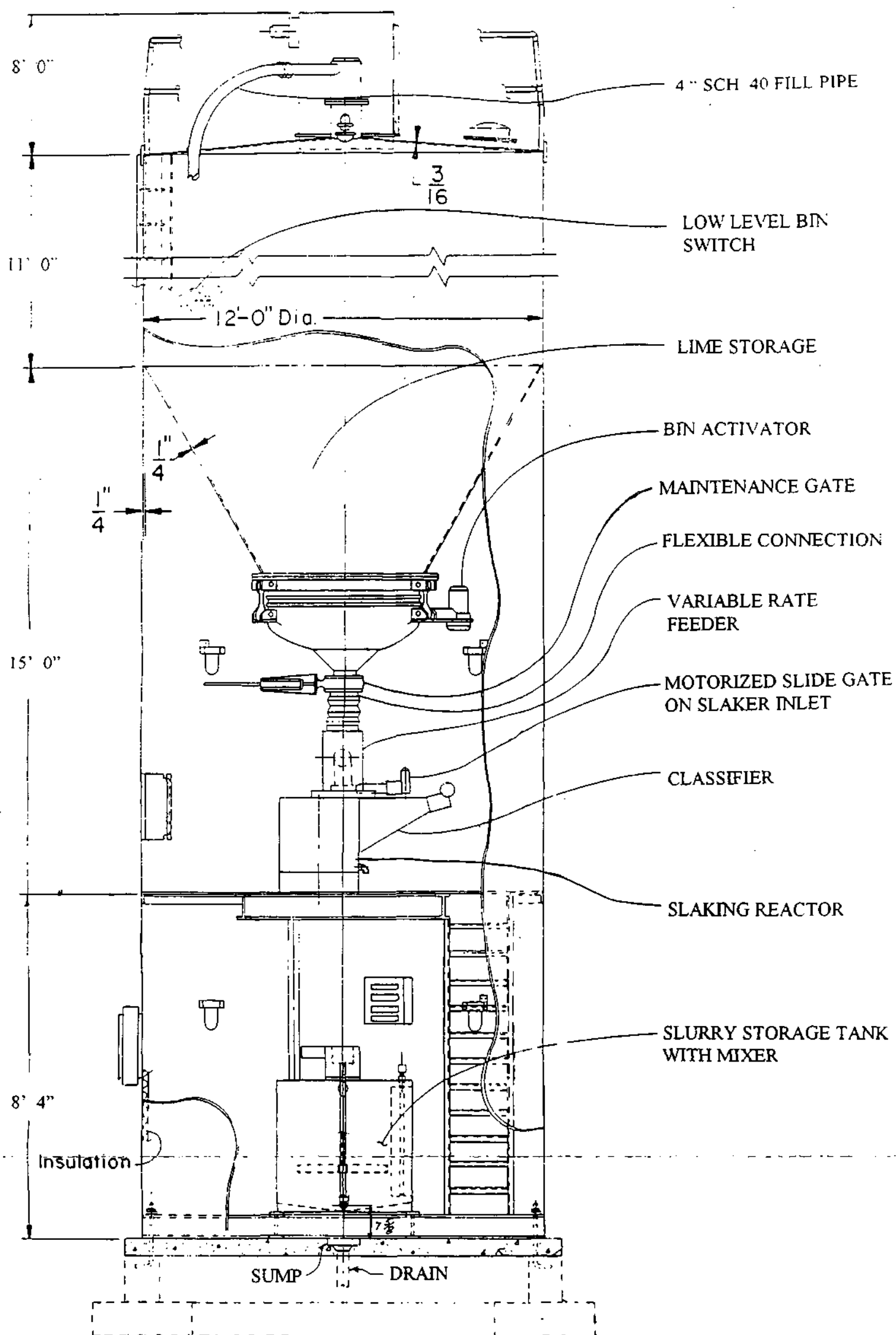
Figure 2.2. Schematic of the lime treatment plant at the St. Louis adit in Rico, Colorado.
Source: Smith & Loveless, Inc. Operation and Maintenance Manual, 1986.

### 2.2.2 CPDES Permit Information

A Colorado Pollution Discharge Elimination System (CPDES) permit was first issued on June 1, 1976 to the Rico Argentine Mining Company for discharge of the St. Louis adit draiange to the Dolores River. The purpose of the permit was to regulate the discharge of toxic pollutants in quantities that might adversely affect the environment. The pollutants in the St. Louis discharge regulated under Permit No. CO-0029793 included cadmium, copper, lead, silver, and zinc. In addition, pH, total suspended and dissolved solids, and the flow rates were limited. Table 2.1 shows the permit requirements.

Since the first issuance, the permit has been transferred to each company who owned the site and is currently held by the Rico Development Company. The current permit was renewed December 30, 1993 for the period of January 1, 1994 through January 31, 1999. Effective February 1, 1995, the 30-day average concentration limits for cadmium, copper, silver and, zinc have been lowered, and the daily maximum concentrations for cadmium, copper, lead, silver, and zinc need only be reported. It should be noted that metals concentrations are total recoverable concentrations. This is the concentration of metals in an unfiltered sample following treatment with a hot dilute mineral acid (EPA Method 3005).

Table 2.1: CPDES Permit No. CO-0029793 Limitations. Permit period is January 1, 1994 through January 31, 1999.

| PARAMETER | LIMITATION | PARAMETER | LIMITATION |
|---|---|---|---|
| Flow, MGD (Avg[a]) | 2.6 | Lead, mg/L (Avg[a]) | 0.0099 |
| Flow, MGD (Max[b]) | report | Lead, mg/L (Max[b]) | report |
| TSS, mg/L (Avg[a]) | 20 | Silver, mg/L (Avg[a]) | |
| TSS, mg/L (Max[b]) | 30 | through 1/31/95 | |
| Oil & Grease, mg/L (Max[b]) | 10 | Jan - Apr | 0.0002 |
| pH, s.u. | 6.5-9.0 | May - July | 0.0006 |
| TDS, mg/L (Quarterly) | report | Aug - Dec | 0.0004 |
| Cadmium, mg/L (Avg[a]) | | beginning 2/1/95 | 0.0001 |
| through 1/31/95 | | Silver, mg/L (Max[b]) | |
| Jan - Apr | 0.0024 | through 1/31/95 | |
| May - July | 0.0055 | Jan - Apr | 0.0004 |
| Aug - Dec | 0.0035 | May - July | 0.0012 |
| beginning 2/1/95 | 0.0004 | Aug - Dec | 0.0008 |
| Cadmium, mg/L (Max[b]) | | beginning 2/1/95 | report |
| through 1/31/95 | | Zinc, mg/L (Avg[a]) | |
| Jan - Apr | 0.0048 | through 1/31/95 | 0.44 |
| May - July | 0.011 | beginning 2/1/95 | 0.237 |
| Aug - Dec | 0.007 | Zinc, mg/L (Max[b]) | |
| beginning 2/1/95 | report | through 1/31/95 | 0.88 |
| Copper, mg/L (Avg[a]) | | beginning 2/1/95 | report |
| through 1/31/95 | 0.03 | | |
| beginning 2/1/95 | 0.024 | | |
| Copper, mg/L (Max[b]) | | | |
| through 1/31/95 | 0.06 | | |
| beginning 2/1/95 | report | | |

[a] 30-day average
[b] Daily maximum
Source: ESA 1995.

## 2.3  Chemistry of Mine Drainage

Extensive literature exists on the subject of mine drainage chemistry and includes comprehensive reviews of acid mine drainage by Hill (1968), Stumm and Morgan (1970, 1981), and Nordstrom (1985), among others. The production of acidic water is common to mining situations where pyrite ($FeS_2$) and other metal-sulfides become exposed to atmospheric conditions. Upon exposure to the atmosphere, sufficient oxygen and water are present to oxidize pyrite according to four elementary reactions (Stumm and Morgan 1981).

The oxidation of pyrite to sulfate produces two moles of acidity for each mole of pyrite oxidized through the reaction:

$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
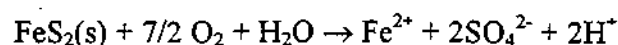
Subsequent oxidation of dissolved ferrous iron results in ferric iron through the reaction:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O$$
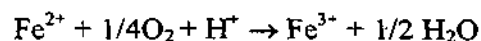
The hydrolysis of ferric iron to insoluble ferric hydroxide releases an additional 3 moles of acidity through the reaction:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
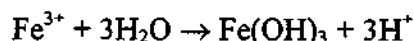
From the combination of these three reactions, it can be seen that the dissolution of one mole of pyrite ultimately leads to the release of four moles of acidity and the evolution of ferric hydroxide:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^-$$

The ferric hydroxide may precipitate as floccule provided the pH is such that its solubility limit has been met. The final elementary reaction is the further oxidation of pyrite by ferric iron:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
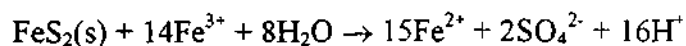
This reaction releases an additional 16 moles of acidity and ferrous iron, which then re-enters the reaction cycle.

In addition to the formation of water with low pH and high iron, acid produced from the above cycle may also dissolve other elements such as, copper, cadmium, zinc, manganese, etc. These elements then enter into the mine drainage. However, this oxidation process would not occur if the pyrite were left in its naturally reducing environment. During mining operations, pyrite ores are exposed to air and ground water flows which subsequently aquires acidity and dissolved metals.

Nonetheless, the specific type of drainage produced by a particular mine is dependent upon the product mined and the nature of the surrounding geologic formations. In the case of the Rico-Argentine mining area, the presence of calcite ($CaCO_3$) and dolomite $MgCa(CO_3)_2$ in addition to pyrite produces acidic drainage which is subsequently buffered to a neutral or near neutral pH (Weir et al. 1983; Pratt et al. 1969; Cross et al. 1905). Hence, the resulting flow from the St. Louis adit may be considered alkaline mine

drainage which generally can be said to have a pH near or greater than neutrality, net alkalinity, high sulfate, significant calcium and magnesium, and a conglomeration of dissolved metals associated with local mining objectives (Hill 1968).

The chemistry associated with naturally occurring limestone raises the pH of the acidic water to neutral levels and introduces bicarbonate alkalinity by consuming hydrogen ions (Stumm and Morgan 1981). The alkalinity-generating and acidity-reducing reactions occur in an order consistent with the solubility products of the minerals involved (Table 2.2), and are as follows (Hedin and Watzlaf 1994):

Highly acidic, metal laden water contacts limestone, which neutralizes the proton acidity ($H^+$). This reaction causes the dissolution of calcite and dolomite. Each mole of calcite and dolomite that reacts produces one and two moles of bicarbonate alkalinity, respectively:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$
$$MgCa(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$
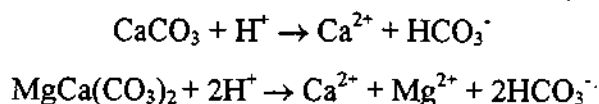
The increased pH level promotes metal hydroxide precipitation and the bicarbonate alkalinity buffers the carbonate acidity produced. The metal hydroxide often remains dispersed as a stable sol:

$$CaCO_3 + 2Fe^{3+} + 6H_2O \rightarrow 3Ca^{2+} + 2Fe(OH)_3 + 3H_2CO_3$$
$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
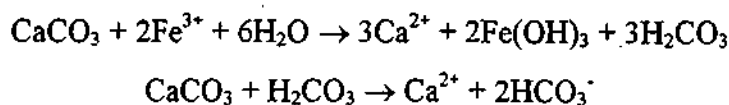
As the pH rises above 4.5, bicarbonate begins to accumulate in appreciable amounts. As bicarbonate concentrations increase, the solubility of metal

carbonates may be exceeded, causing precipitation of siderite (FeCO₃), rhodochrosite (MnCO₃), and cerussite (PbCO₃):

$$CaCO_3 + Fe^{2+} \rightarrow Ca^{2+} + FeCO_3\downarrow$$
$$CaCO_3 + Mn^{2+} \rightarrow Ca^{2+} + MnCO_3\downarrow$$
$$CaCO_3 + Pb^{2+} \rightarrow Ca^{2+} + PbCO_3\downarrow$$
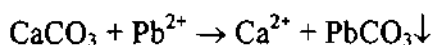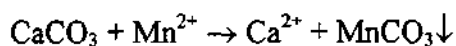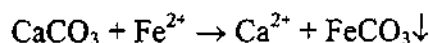
With each of these reactions, calcium is released into solution. As the concentration of calcium increases, the potential for gypsum ($CaSO_4 \bullet 2H_2O$) precipitation increases:

$$CaCO_3 + SO_4^{2-} + 3H_2O \rightarrow CaSO_4 \bullet 2H_2O\downarrow + OH^- + HCO_3^-$$

Table 2.2: Solubility product constants of minerals often found in mine waters.

| MINERAL | REACTION | Log K[a] |
|---|---|---|
| Calcite | $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$ | -8.35 |
| Dolomite | $MgCa(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ | -16.7 |
| Ferric Hydroxide | $Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$ | -38.8 |
| Cerrusite | $PbCO_3 \leftrightarrow Pb^{2+} + CO_3^{2-}$ | -13.1 |
| Siderite | $FeCO_3 \leftrightarrow Fe^{2+} + CO_3^{2-}$ | -10.7 |
| Rhodochrosite | $MnCO_3 \leftrightarrow Mn^{2+} + CO_3^{2-}$ | -10.4 |
| Gypsum | $CaSO_4 \bullet 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$ | -4.62 |

[a] K is equal to the product of the activities of the product ions, and the more negative the value the more likely the solid will precipitate.

The precipitation of minerals as the mine water flows through the limestone usually results in fine particles suspended in solution. This colloidal suspension provides an efficient means of metal transport, as the enormous surface area of colloidal particles makes reactions at the solution-particle interface inevitable. Thus, a general understanding of this surface chemistry is warranted.

The bulk of the literature on adsorption in aquatic systems deals mostly with metal oxides, principally those of iron. Moreover, it is probably safe to assume that the majority of colloids formed in acid mine drainage are indeed iron oxides, since the production of acidic drainage is due primarily to the oxidation of iron pyrite ores.

The most important characteristics of colloids are the high ratio of surface area to volume, and the resulting voluminous surface charge. Colloidal particles have a diameter in the size range of $10^{-2}$ $\mu$m to 10 $\mu$m, and may exhibit surfaces areas as large as 600 square meters per gram (Krauskopf and Bird 1995). This large surface area provides an abundance of surface charge for sorption and ion exchange of metals dissolved in solution.

The charge of a colloid will dictate the sorption chemistry involved at the surface, and obviously, electrostatically charged surfaces must attract ions of opposite charge. The surface of a metal oxide colloid can exhibit either a positive or a negative charge, depending on whether the metal (M) or the lignand (OH) is in excess at the surface ($\equiv$) (Morel 1983). Stumm and Morgan (1981) and Salomons and Förstner (1988) provide a simplistic understanding of the various reactions that can occur at the surface, and Figure 2.3 illustrates these reactions.

The charge at the metal oxide surface results, in part, from proton transfers at an amphoteric surface:

$$\equiv M\text{-}OH_2^+ \leftrightarrow \equiv M\text{-}OH + H^+$$
$$\equiv M\text{-}OH \leftrightarrow \equiv M\text{-}O^- + H^+$$
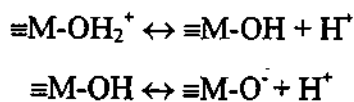
In addition, protons and metal ions compete with each other for available coordinating sites:

$$\equiv M\text{-}OH + M^{Z+} \leftrightarrow \equiv M\text{-}OM^{(Z\text{-}1)} + H^+$$

$$\begin{matrix} \equiv M\text{-}OH \\ | \\ \equiv M\text{-}OH \end{matrix} + M^{Z+} \leftrightarrow (\equiv M\text{-}O)_2 M^{(Z\text{-}2)} + 2H^+$$
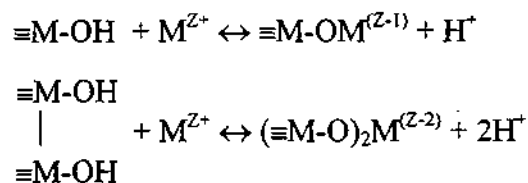
Depending on the charge (Z) of the metal, the resulting surface charge may be positive, negative, or neutral.

In addition to the adsorption of dissolved metals, the presence of electrolytes causes the colloid to coagulate, prompting the particles to settle out or flocculate. Flocculation also occurs by the addition of a colloid that is simultaneously adsorbed to the surfaces of adjacent particles, linking them together to form a microgel (Krauskopf and Bird 1995). Figure 2.4 depicts this flocculation process.

Although this is a crude representation of a very complex process, it illustrates a very important point. Metals in solution can adsorb onto existing solid particles and coprecipitate with them. Hence, coprecipitation becomes a secondary metal removal mechanism through heterogeneous reactions.

Surface                          Solution                    Surface
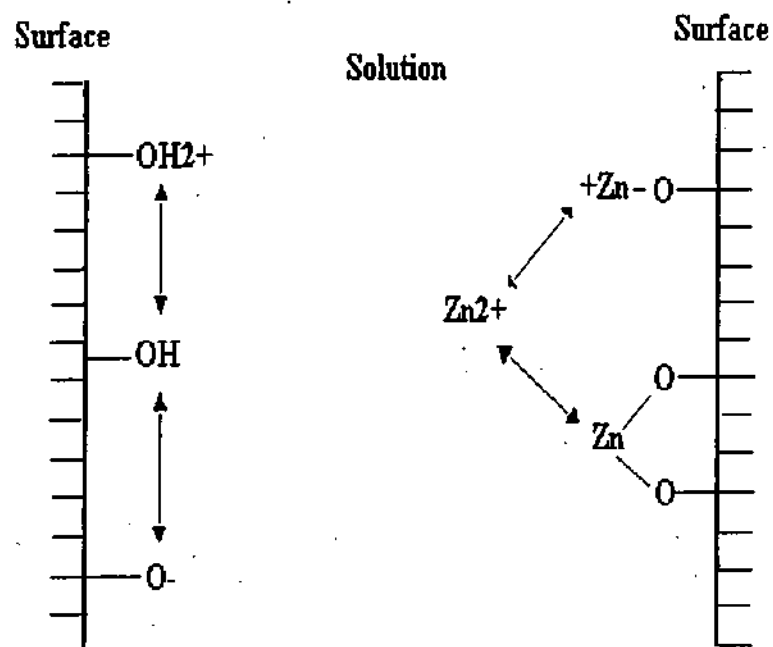


Figure 2.3: Illustration of metal oxide surface reactions.
Source: Stumm and Morgan 1981.
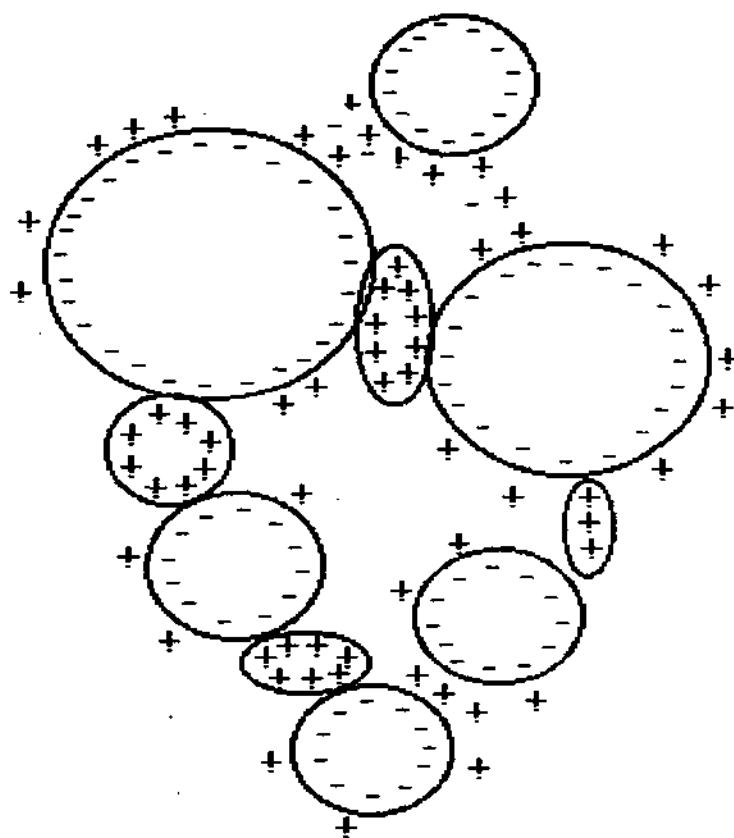
Figure 2.4: Schematic representation of colloid particles flocculating together to form a microgel.
Source: Krauskopf and Bird 1995.

## 2.4 Treatment Options

The treatment of mine drainage refers to chemical and physical procedures used to improve drainage quality, and there is an increasing need for economically viable and environmentally sound methods to achieve this. Furthermore, technologies must be capable of achieving treatment levels prescribed by regulatory constraints such as those in CPDES permits.

The conventional approach to treat mine drainage is chemical neutralization and precipitation using lime. While sometimes effective, this traditional pump-and-treat method is often costly and inefficient. In addition to producing large volumes of unstable metal hydroxide sludges which may be labeled hazardous and therefore expensive to dispose of, the long term commitment associated with treating drainage which could persist over hundreds of years is prohibitive. Although many remediation technologies have been developed for the removal of metals from mine drainage, the desire to utilize existing equipment and ponds, in addition to the need to limit operation and maintenance costs has dictated the treatment options considered for the St. Louis adit. The technologies outlined here include an innovative approach to lime precipitation, sulfide precipitation using biogenic $H_2S$, and constructed wetlands.

## 2.4.1 Conventional Lime Treatment Process

In conventional lime treatment processes, lime $(Ca(OH)_2)$ or quicklime $(CaO)$ is used as a precipitant in the removal of metals as insoluble metal hydroxides (Krishnan et.al. 1994). The precipitated solids are then removed from the treated water by settling.

The general reaction that occurs to produce insoluble metal hydroxides is illustrated by the following equation for the precipitation of a divalent metal (Chung 1989):

$$M^{2+} + Ca(OH)_2 \rightarrow M(OH)_2 + Ca^{2+}$$
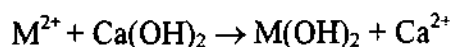
The effluent concentration levels achievable by hydroxide precipitation are dependent on the metals present and the pH. Each metal precipitate has a pH at which its solubility is minimized. By adjusting the solution pH into the range of a metal's minimum solubility, the metal is substantially removed. However, the minimum solubility pH for each metal is not concurrent (ibid.). Table 2.3 lists the pH at which the minimum solubility of some metal hydroxides found in mine drainage would occur (Stumm and Morgan 1981, Chung 1989, Krishnan 1994).

Table 2.3: The pH at which the minimum solubility of some metal hydroxides found in mine drainage would occur.
Source: Stumm and Morgan 1981, Chung 1989, and Krishnan 1994

| METAL | pH, s.u. |
|---|---|
| Cadmium | 11.2 |
| Copper | 8.8 |
| Iron (III) | 8.0 |
| Lead | 9.2 |
| Zinc | 9.0 |

In addition to the optimum pH for minimum solubility differing, metal hydroxides are amphoteric, ie. capable of solubilizing at a high and a low pH. Therefore, increasing the pH to 11.2 to precipitate cadmium hydroxide would result in the other metals dissolving back into solution. Hence, the optimum pH for a mixture of metals must be determined experimentally, taking into account discharge standards since the optimum pH cannot be met for all.

Following the precipitation of the metal, the metal floc must be separated from the water. This is usually accomplished by gravity separation in a pond or clarifier, after which the clarified water is drawn off. The resulting sludge from this process is voluminous, and presents problems when long-term treatment is required. The sludge, which rarely contains more than 2.5% solids, consumes vast quantities of necessary storage space in a relatively short period of time (Murdock, et al 1994). Furthermore, sludge stability is questionable, and redissolution of precipitated metals is a concern. Those sludges that exceed the Toxicity Characteristic Leaching Procedure (TCLP)[3] concentration limits for extractable metals are deemed hazardous and must be disposed of in RCRA certified disposal facilities[4] (Reinhardt 1989, Corbitt 1990). Table 2.4 provides the limits for TCLP extractable metals (ibid.).

The fact that the sludge may be considered hazardous is significant because sludge disposal at a RCRA facility costs about $220/ ton compared to $28/ton for non-hazardous disposal (McLaughlin, et al 1995). Therefore, it is obvious that the sludge produced from this process provides the motivation needed to seek out innovative alternatives for mine drainage remediation.

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[3] The degree of resistance of the mixture to leaching by the procedure set forth in the Code of Federal Regulations, 40 CFR Part 261 Appendix II. The Code of Federal Regulations is published by the Environmental Protection Agency (EPA).
[4] The Resource Conservation and Recovery Act (RCRA) of 1976 is the primary legislation controlling hazardous waste management, and treatment, storage, and disposal facilities (TSDF) are defined in 40 CFR 260.10.

Table 2.4:  Concentration Limits for TCLP extractable metals.
Source: Reinhardt 1989 and Corbitt 1990.

| METAL | TCLP LIMIT, mg/L |
|---|---|
| Arsenic | 5.0 |
| Barium | 100.0 |
| Cadmium | 1.0 |
| Chromium | 5.0 |
| Lead | 5.0 |
| Mercury | 0.2 |
| Selenium | 1.0 |
| Silver | 5.0 |

2.4.2  Innovative Approaches To Lime Treatment

Despite its shortcomings, there are valid reasons for the dominance of chemical neutralization and precipitation using lime for the removal of metals from mine drainage. The chemistry of precipitation is controllable and predictable, and lime is widely available, inexpensive, and easily handled.  Consequently, innovative modifications of conventional lime treatment processes have been developed to help overcome its deficiencies.

There are essentially two types of innovations that have been developed.  The first is the modification of the physical processes involved in lime precipitation, and the second is the is a modification of the chemistry of lime precipitation.  Furthermore, a combination of both chemical and physical changes has been realized.   The primary objective of the

studies conducted with these innovations consisted of improving effluent metals concentrations, while altering the sludge characteristics.

The early examinations of novel approaches to lime precipitation began with investigations of improving the physical process of sludge densification. In 1980, the drainage from the Argo Mine Tunnel in Idaho Springs, Colorado was selected for the testing of a sludge concentrating system developed by Colorado Mining and Chemical, Ltd. The purpose of this research and demonstration project, initiated through the Colorado Inactive Mine Reclamation Program, was to determine the effectiveness of neutralization followed by precipitate concentration and filtration as a method for removing trace elements and acidity from the drainage (Resource Recovery Demonstration Project 1980). Results indicated that the process was only somewhat effective for removing trace elements from the drainage while significantly consolidating the metal hydroxide sludge (ibid.).

Another sludge densification study was conducted in 1982 by The Colorado School of Mines Research institute (CSMRI), on drainage from the St. Louis adit in Rico, Colorado. This was a bench-scale test designed to simulate the high-density sludge process originally developed by P. D. Hostenbader and G. F. Haines of Bethlehem Steel Corporation (CSMRI 1982). This approach is essentially a lime precipitation process which separates the precipitate from the clean effluent using a mechanical clarifier. A portion of the sludge is then recycled and additional lime is added to this recycled sludge. Results from the study indicated an increase in percent solids in the sludge, from 2% after simple gravity sedimentation to as high as 40% after several days of continuous sludge recirculation. After 11 recycles, the sludge volume was less than one third of that obtained with simple precipitation, but the process exhibited only marginal effectiveness in removing trace metals (ibid.).

By the 1990's the emergence of chemical modifications to lime treatment were being explored, and a study conducted by the U.S. Bureau of Mines in 1991 revealed that

the addition of copolymers, combinations of polymers, guars, and gums in conjunction with lime all reduced the concentrations of cadmium and lead to <0.01 ppm and 0.01 ppm levels, respectively (Carter and Scheiner 1991). This study indicates that the addition of flocculants, such as polymers, in addition to lime, greatly increased the number of surface sites available for coprecipitation of dissolved metals. These activated molecules also have many charge sites that attract colloidal or suspended solid particles of the opposite charge, thus, forming a larger floc of agglomerated solids which settle, filter, and dewater at a substantially increased rate (ibid.).

To further enhance the lime precipitation process, a combination of both chemical and physical modifications has been developed. A paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, in 1994 describes the application of a high density sludge (HDS) process, similar to the process originally developed by the Bethlehem Steel Corporation. However, HDS utilizes both sludge recycle and the addition of polymers for improved flocculation (Murdock, et al 1994). Figure 2.5 illustrates the HDS process.

Several full-scale plants have been established in Canada and the United States since 1980 and include: The Sullivan Mine of Cominco Ltd. in British Columbia, Canada, the Brunswick Mining and Smelting Company in New Brunswick, Canada, and the Glenbrook Nickle Company in Oregon. These full-scale plants demonstrate the success of the HDS process, which has been shown to treat up to 22 million gallons of mine drainage per day, producing a stable hydroxide sludge containing 20% to 40% solids, and effectively removing trace metals to treatment specifications (Murdock, et al. 1994).
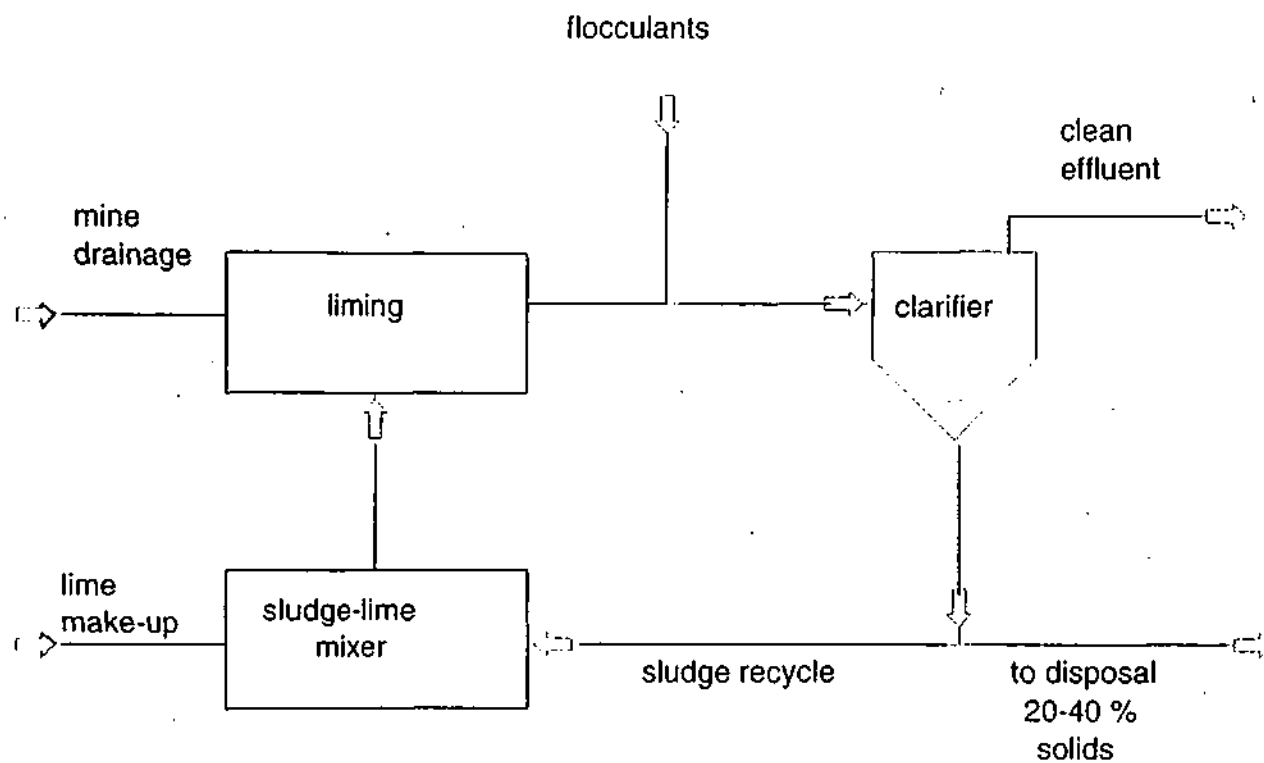
Figure 2.5. Process flow diagram for the high density sludge process. Individual processes may vary from this basic design.
Source: Murdock, et al. 1994.

## 2.4.3 Sulfide Precipitation Using Biogenic H₂S

Sulfide precipitation using biogenic $H_2S$ has several potential advantages as an alternative to hydroxide precipitation. The solubilities of metal sulfides are considerably lower than those of corresponding metal hydroxides. Furthermore, unlike metal hydroxides, metal sulfides are not amphoteric, and continue to precipitate as the pH of the solution increases (Chung 1989, de Vegt and Buisman 1993). Table 2.5 demonstrates the substantial difference between metal hydroxide and metal sulfide solubilities.

Table 2.5: Theoretical solubilities of various metal hydroxides and metal sulfides in pure water at a pH of 7.0.
Source: de Vegt and Buisman 1993.

| METAL | SOLUBILITY in mg/L as HYDROXIDE | SOLUBILITY in mg/L as SULFIDE |
|---|---|---|
| Cadmium | $2.35 \times 10^{-3}$ | $6.73 \times 10^{-10}$ |
| Copper | $8.42 \times 10^{-4}$ | $5.83 \times 10^{-18}$ |
| Iron | $8.91 \times 10^{-1}$ | $3.43 \times 10^{-5}$ |
| Lead | 6 | $5.48 \times 10^{-10}$ |
| Silver | 13.3 | $7.42 \times 10^{-12}$ |
| Zinc | 1.1 | $2.31 \times 10^{-7}$ |

The extremely low solubilities of sulfide metals results in improved metal concentrations in the effluent and a more stable sludge. In addition, the resulting sludges are suitable for metals reclamation which could offset treatment costs (Corbitt 1990, Hammack, et al. 1994, Rowley, et al. 1994).

The use of biologically produced hydrogen sulfide ($H_2S$) gas is particularly appealing in the remediation of mine drainage. Mine water usually contains high sulfate

($SO_4^{2-}$) concentrations and supplies the necessary ingredient for the production of $H_2S$. Consequently, this process serves the dual purpose of reducing sulfate and metal concentrations in the water.

Many investigators have developed processes using sulfate reducing bacteria to treat metal contaminated mine waters (Rowley, et al. 1994, deVegt and Buisman 1993, Hammack, et al. 1994). Although each process may vary in its specific design, they all subscribe a similar technological theory.

In general, the technology consists of a biological process and a solids precipitation process. DeVegt and Buisman (1993) describe the process in the most elementary terms.

In a bioreactor, the $H_2S$ needed for water treatment is generated by sulfate reducing bacteria via an oxidation-reduction reaction. The SRB anaerobically oxidize organic matter present in the water while producing a simultaneous reduction of sulfate to hydrogen sulfide gas:

$$SO_4^{2-} + \text{organic matter} \xrightarrow{\text{bacteria}} H_2S + \text{oxidized organic matter}$$
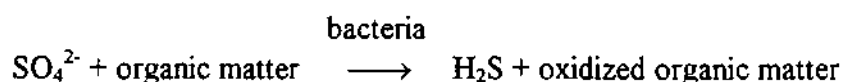
The organic matter acts as an electron donor in this reaction, and when oxidized provides alkalinity to the system. However, mine drainage seldom contains sufficient organic compounds, and it becomes necessary to add an electron donor. Some examples of electron donors are ethanol and organic wastes. The $H_2S$ generated reacts with metals present in the wastewater to form metal sulfide precipitates:

$$M^{2+} + H_2S \rightarrow MS\downarrow + 2H^+$$

The proton acidity evolved from this reaction causes a decrease in the water pH that may not be consumed by the alkalinity produced in the prior step. Hence, it often becomes necessary to make pH adjustments to meet effluent standards. In any case, the sludges produced are often amendable to metal recovery in a smelter and this may help offset treatment costs.

Several biogenic $H_2S$ treatment systems have been tested, or are currently in full scale operation. The first commercial-scale treatment plant began operation in May 1992 at the Budelco B.V. Mine smelter site in the Netherlands. The plant, developed by the Dutch company Paques B.V., was designed to treat approximately 1.8 MGD of contaminated water containing 50 mg/L Zn and 0.1 mg/L Cd using a bioreactor and a single precipitator-clarifier unit (Figure 2.6) (de Vegt, et al. 1993). Plant performance data indicates that sulfate concentrations were reduced by 80%, from an influent concentration of 1000 mg/L to an effluent concentration of 200 mg/L. In addition, zinc and cadmium were removed with an average efficiency of 99.7 %. The effluent zinc concentration were reported to be 0.05 - 0.015 mg/L (ibid.).

The United States Bureau of Mines (USBM) recognized the potential of this process to recover metals from mining waste streams which often contain several different metals, and performed bench-scale tests on a system designed to selectively recover valuable metals (Hammack, et al. 1994). The system configuration consisted of a bioreactor and three precipitator-clarifier units. By performing pH adjustments between each stage, three separate sludges were produced that may be suitable for metal recovery at existing smelters. Hammack, et al. (1994) reported that the bench-scale treatment system was effective in the removal of Cu, Zn, Co, Ni, Fe, Mn, and Al. In addition, the system produced a copper concentrate containing 33% Cu, and a zinc concentrate containing 28% Zn (ibid.).
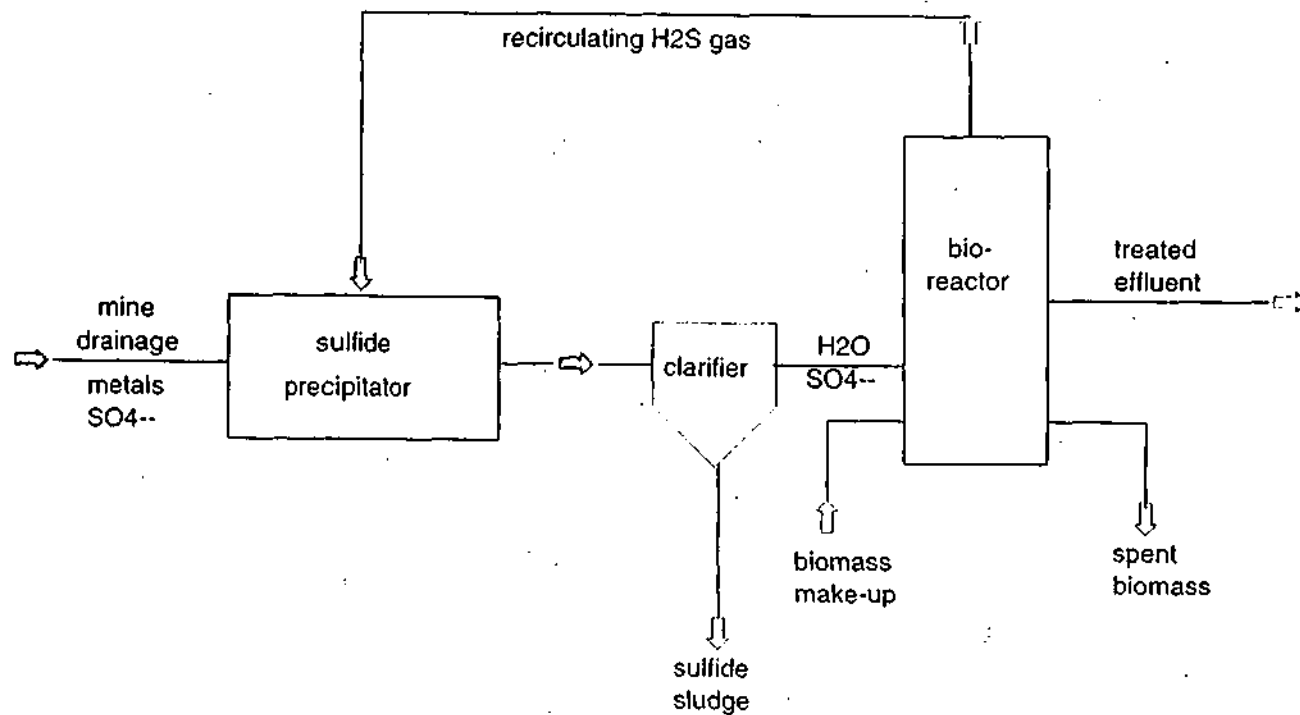
Figure 2.6. Process flow diagram for the biogenic $H_2S$ sulfide precipitation process, with a single precipitator-clarifier. Individual processes may vary from this basic design.
Source: De Vegt, et al. 1993

A pilot-scale study of a treatment process similar to the bench-scale process analyzed by the USBM was conducted by the Triton Development Corporation of Vancouver, British Columbia (Rowley, et al. 1994). The process, called the Biosulfide Process, again uses three separate precipitator-clarifier units and pH adjustments between each. Rowely, et al. (1994) reported that the pilot-scale system ran continuously for 75 hours, maintained an average sulfate reduction of 85%, and exceeded discharge requirements for copper (<0.05 mg/L) and zinc (<0.2 mg/L) (ibid.).

Results from these three studies demonstrate that a biogenic $H_2S$ process is a potential alternative to conventional mine drainage treatment. In addition to successfully treating waste waters, this process isolates potentially valuable metal sulfides which could be sold to offset operating costs.

## 2.4.4 Constructed Wetlands

Wetlands have been used for the disposal and treatment of contaminated water since the 1950's in a wide variety of applications such as municipal wastewater, storm water runoff, and agricultural non-point source runoff (Reed, et al. 1995). However, within the past several years, there has been increased interest in the use of wetlands to treat mine drainage when it was observed that wetlands can act as a sink for metals (Gersberg, et al. 1985, Weider 1988, Skousen, et al. 1992, Whiting, et al. 1994, Eger, et al. 1994, Dretz, et al. 1994, Reed, et al. 1995, Watzlaf and Hyman 1995). There are two basic types of constructed wetlands; aerobic and anaerobic. Table 2.6 provides a comparison of aerobic and anaerobic wetlands. Regardless of the type of wetland, there are several physical, chemical, and biological mechanisms that occur in wetland systems to reduce metal concentrations. The major mechanisms are ion exchange, sorption, and

precipitation by geochemical and microbial oxidation and reduction (Boto and Patrick 1979, Damman 1979, Dollhopf, et al. 1988, Walton-Day 1991).

In aerobic wetlands, the surface is exposed to the atmosphere. In addition, the bed contains aquatic vegetation, a layer of soil to serve as a rooting media, and a liner to protect the groundwater. The water depth ranges from a few centimeters to 0.8 meters or more, and design flows range from 100 gallons per day to 20 million gallons per day (Reed, et al. 1995). The typical retention time in aerobic wetlands is 5 to 10 days, where the oxidation of metals to form oxide precipitates is emphasized, for example:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
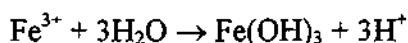
This reaction has the tendency to lower the effluent pH due to the release of proton acidity during the hydrolysis of metals. In alkaline mine drainage, this effect would be buffered. However, buffering agents may need to be added when treating acidic mine drainage (Watzlaf and Hyman 1995). Aerobic cells are appropriate for the removal of iron, aluminum, manganese, arsenic, cyanide, and mercury (Gusek 1995).

In anaerobic wetlands, the excavated basin is filled with porous material, and the water level is maintained below the top of this material. This creates reducing conditions where sulfide metals are precipitated in a reaction mechanism similar to that explained in the biogenic $H_2S$ process earlier:

$$SO_4^{2-} + \text{organic matter} \longrightarrow H_2S + \text{oxidized organic matter}$$

$$M^{2+} + H_2S \rightarrow MS\downarrow + 2H^+$$
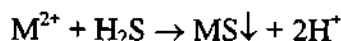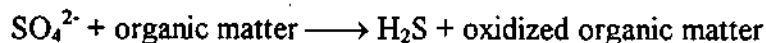
Because the oxidation of organic matter creates alkalinity, anaerobic wetlands have a tendency to increase the effluent pH creating neutral or near neutral conditions (Watzlaf

and Hyman 1995). The depth of the porous material is usually 1 to 1.5 meters, and a retention time of 3 to 5 days is recommended (Reed, et al. 1995). Anaerobic cells are typically filled with an organic substrate inoculated with manure, and are ideal for removing copper, lead, zinc, mercury, cadmium, aluminum, and sulfate (Gusek 1995).

Constructed wetlands are man-made simulations of natural wetland systems which have the potential of being more effective because the hydraulics and retention times can be controlled and optimized, and the capability for the remediation of mine drainage using constructed wetlands has been verified in a number of studies (Whiting, et al. 1994, Hellier, et al. 1994, Dietz, et al. 1994). Furthermore, constructed wetlands provide the possibility to treat mine drainage without the continual addition of chemicals or neutralizing agents, thus, reducing operation and maintenance requirements.

Table 2.6: A comparison of aerobic and anaerobic constructed wetlands.

| AEROBIC | ANAEROBIC |
|---|---|
| Surface flow of water | Subsurface flow of water |
| Exhibits oxidizing conditions | Exhibits reducing conditions |
| Produces oxide precipitates | Produces sulfide precipitates |
| Chemical process increases proton acidity which may lower the effluent pH | Chemical process increases alkalinity which may increase the effluent pH |
| Effective in removing Fe, Al, Mn, As, Cyanide and Hg | Effective in removing Cu, Pb, Zn, Hg, Cd, Al, and Sulfate |
| Depth ranges from a 0.03 m to 1 m | Depth ranges from 1 m to 1.5 m |
| Retention time ranges from 5 to 10 days | Retention time ranges from 3 to 5 days |

## 2.5 Sludge Management

Sludge management can be described as directing or controlling the production, treatment, disposal, or reuse of sludge. The sludge is defined as a waste byproduct of mine drainage treatment, and contains heavy metals which may be considered hazardous. The conventional method of treatment for mine drainage is lime precipitation. This process, which is very effective in removing metals from water, produces large quantities of heavy metal laden sludge. The sludge, if considered hazardous, must be disposed of in hazardous waste landfills which cost about $220/ ton compared to $28/ton for non-hazardous disposal (McLaughlin, et al 1995).

Sludge disposal may very well be the most expensive aspect of mine drainage remediation. Hence, the selection of mine drainage treatment options must always take into consideration the management of inherent byproducts. There are two general avenues to the management of sludge; sludge reduction, and sludge reuse. Metal recovery from sludge produced in mine drainage treatment may also be considered a category. However, the nature of mine drainage discourages the use of such technologies.

Metal recovery technologies are processes that recover metals from both wastewater and sludge, and include electro-separation, membrane separation, leaching, and ion exchange (Krishnan, et al 1994). Processes such as these are most often used to recover metals from wastewaters produced in the electroplating and electronic industries, where extremely high and relatively pure concentrations occur. These are not stand alone technologies, and high capital and operating costs incurred by these technologies may not merit their use for the treatment of mine drainage. Mine drainage is typically dilute in valuable metals and contains a mixture of metals that would be difficult to recover. An exception to this supposition may be the metal sulfide sludges produced in the biogenic $H_2S$ process described earlier. These sludges, when separated selectively through this process contain relatively pure concentrations of metals which can be recovered at

smelters. Both pilot-scale and commercial-scale biogenic $H_2S$ treatment plants have produced sludges containing copper and zinc concentrates that could be processed at existing smelters ( Hammack, et al 1994, Rowley, et al. 1994).

Since the amount of sludge produced has a direct impact on disposal costs, a key component of sludge management is reduction. The large amount sludge produced from conventional lime treatment plants often contains only 2% to 6% solids (Murdock, et al 1994). Hence, dewatering the sludge could result in a dramatic decrease in the total volume produced.

Dewatering consists of removing as much water from the sludge as possible so that the resulting volume to be processed is minimized. Achieving the maximum amount of water removal usually requires both the chemical addition of thickeners and the application of a mechanical dewatering device. The chemicals most often added are high molecular weight polymers which provide a massive amount of active surfaces that attract colloidal or suspended solid particles of the opposite charge, thus, forming a larger floc of agglomerated solids which settle, filter, and dewater at a substantially increased rate (Carter and Scheiner 1991). Moreover, the high density sludge process (HDS) discussed earlier also enhances the thickening process. The sludge recycle provides a surface for the metals to precipitate on, and the solid particles grow each time they are recycled. Consequently, the particles may attain sizes up to five times larger than those in conventional sludges, producing sludges with 4% to 8% solids (Mosher 1994).

Once the sludge has been thickened, mechanical devices are used to further increase the solids content. Typical mechanical devices include vacuum filters, pressure filters, belt filters and centrifuges (Reynolds 1982, Vesilind, et al. 1995).

With the combination of thickening and mechanical dewatering, the resulting solids content in sludges can be as high as 50 percent. According to John Mosher of the Colorado School of Mines and Hazen Research Inc., Asarco employs the HDS process in conjunction with a pressure filter to treat the Yak Tunnel/California Gulch mine drainage

near Leadville, Colorado, and attains a solids range from 20% to 40% (Mosher 1994). Furthermore, McLaughlin Water Engineers, Ltd designed and built a water treatment plant in Minturn, Colorado to treat drainage from the Eagle Mine. This process employs a unique combination of chemical addition, sludge thickening, and dewatering using a filter press. Solids content in sludges from this process are consistently 50 percent (McLaughlin, et al. 1995).

The reuse of sludge produced from the treatment of mine drainage applies primarily to sludges created from lime neutralization and precipitation. Innovative methods have been found for dealing with such wastes. For example, "Asarco's California Gulch water treatment plant in Colorado uses wastewater treatment sludge as a smelter feed stock, recovering incidental saleable metals, and producing non-hazardous products" (Mosher 1994). In a thermal process, developed by the Nihon Cement Company in Japan, sludge rich in silicates and calcium oxides is used to make cement (Fouhy and Moore 1994). Provided that 30 % of the total water content has been removed, these sludges can be reused instead of disposed of in costly landfills. Consequently, the concerns about disposal costs transfer to concerns about shipping costs. If smelters or cement operations are not locally available, shipping costs may become prohibitive.

## 2.6 Modeling Methods

When evaluating a site for remediation, relatively little information is available to assess the appropriate technology to be employed and the ultimate fate of the contaminants. Aside from historical examples of processes currently in use, the tools needed to predict the applicability of a particular process to a specific site are limited.

While geochemical modeling is well established in this field, process modeling from a chemical engineering standpoint is not. This chemical engineering approach to a

traditionally geochemical problem could provide an additional tool for selecting and designing an appropriate process for site specific remediation. Since the accurate prediction of the potential applicability of a technology is of concern to both responsible parties and regulatory agencies, it is the intent in this section to discuss relevant aspects of the models used and investigated in this research.

## 2.6.1 MINTEQA2 Geochemical Modeling

The MINTEQA2 model is a quantitative tool for determining the chemical equilibrium properties of natural systems. The properties that MINTEQA2 predicts includes aqueous phase speciation, adsorption, solid phase saturation states, and the precipitation and dissolution of metals (Allison, et al 1993).

The model uses mathematical tools such as the solubility product constant to determine the saturation state of precipitates, the Van't Hoff equation to correct the equilibrium constants for temperature variations, the Debye-Hückel expression for calculating activity coefficients, and numerous adsorption models for predicting surface reactions (ibid.) With the combination of mass balance calculations and equilibrium saturation indices, dissolved, precipitated, and adsorbed species can be determined.

## 2.6.2 ASPEN Plus Process Modeling

ASPEN Plus is a process modeling and simulation tool used by engineers to model processes for which there is a continuous flow of materials and energy. The model provides a complete representation of the performance of a process, including the composition, flow, and properties of all streams and process units involved (Aspen Tech

1993). Furthermore, this model has the capability to analyze electrolyte systems including predicting dissolved and precipitated species. The solubility product constants, the electrolyte NRTL and Bromley-Pitzer activity coefficient models, as well as various transport property models, thermodynamic models, and equation of state models (which are much too numerous to list) are among the many mathematical tools used to simulate electrolyte processes (Aspen Tech 1994).

Although this model is not specifically designed to simulate processes occurring in mine drainage treatment, the mathematical tools and the extensive data bank available provide the necessary ingredients for this purpose. Once the process flow sheet has been defined and the chemical components, chemical reactions, thermodynamic properties and transport properties are specified, the model can aid in interpreting data, performing sensitivity analysis and optimizations, and studying alternative processes.

The most important quality that any model should possess is that of being accurate. The model should properly reproduce the basic physical phenomenon that is being approximated. Therefore, comparisons with analytical concentrations observed at the actual site will give indications of how reliable and accurate a given model will be.

Chapter 3

EXPERIMENTAL

Sampling activities at the St. Louis settling ponds were conducted in August of 1995. The purpose of the field investigation and subsequent analysis was to gather sufficient data to provide a general characterization of the site, and to support modeling efforts.

## 3.1 Sampling Strategy

The decisions made regarding sampling locations and types of samples taken were based on the results of previous studies, as well as the selection of suitable control volumes for material balance modeling. Two possible outcomes for metals present at this site were determined. The metals could either remain at their present location, or they could be carried elsewhere by transport processes. Based on this premise, two control volumes were selected. The first control volume included ponds 11, 12, 14, 15, 18, and the water treatment plant. The second included ponds 5, 6, 7, 8, and 9.

## 3.1.1 Type and Location of Samples

Sampling locations were chosen to simplify the problem of determining chemical transport rates into and out of the control volumes, as well as the concentrations within the control volumes. The field work conducted included measurements of flow rates, sampling of surface waters at various locations, and sampling of the sediment and pore

waters in several of the ponds. Features of the settling ponds and sampling locations are shown in Figure 1.2.

Flow rates were measured at the St. Louis adit, influents to ponds 9 and 18, and effluents from ponds 5 and 11. Surface and subsurface water samples were taken at the adit, and ponds 5, 9, 11, and 18. Subsurface samples where taken at the liquid-solid interface. Sediment core sample were obtained from ponds 5, 9, 11, and 18. The cores were segmented based on defining characteristics of each core. Pore waters were then extracted from each segment.

Further analysis of the site during the field work indicated the need for four additional surface water samples; two from the geothermal vents located in ponds 5 and 6, and two from a channel of the Dolores River located on the west side of pond 18. It was decided that the two geothermal vents could be providing significant contributions to the transport of chemicals into the control volume. The decision to sample the channel was based on the presence of oxidized iron-rich stream bed precipitates, characterized by their bright orange color, indicating possible seepage from pond 18, see Figure 3.1. One sample was taken upstream from pond 18, where no precipitate was visible. The other sample was taken down stream from pond 18, where the channel re-enters the river.

Figure 3.1. Channel of the Dolores River west of pond 18. The bright orange precipitate indicates possible seepage from pond 18.

### 3.1.2 Sampling Sequence

A sampling sequence plan was developed to help prevent cross contamination. All flow rates were measured first, starting at the pond 5 effluent and working up to the adit. Surface water samples were taken in the same sequence as the flow rates, except for the river and geothermal vent samples which were taken after sampling was completed. In each case, field analysis was conducted and samples were preserved prior to moving on to the next location. Coring started with pond 5 and finished with pond 18. Prior to each coring event, water and sediment depths of each cored pond were determined using a calibrated pole and raft. After each core was pulled, it was immediately segmented and individual samples were sealed and preserved.

### 3.2 Flow rate Measurements

Flow rates were measured using one of three different techniques; the simple float method, the bucket and stop watch method, and the Manning equation, depending on the nature of the flow. The float method was used to measure the flow rates of the effluents from the adit and pond 5. Both of these locations consisted of concrete channels that were easily measured. In each case, the cross-sectional area, $A_{cs}$, in the concrete channel was measured and a floating object (60 ml polyethylene sampling bottle) was timed as it traveled a measured distance, L. The cross-sectional area was measured by two different people, using either a pole calibrated to the nearest inch or a tape measure, depending on the depth of the channel. Ten trials were performed at each location and timed using a stop-watch. The results of the ten trials were then averaged and the flow rates were determined by the following equation:

$$Q(ft^3/s) = A_{cs}(ft^2) \, L(ft)/t(s)$$

The flow of water into pond 18 consisted of four pipes. One 17.5 inch I.D. pipe, two 4 inch diameter pipes and one 13.5 inch diameter pipe, all made of plastic (Figure 3.2). The bucket and stop-watch method was used to calculate the flow rates from the three smaller pipes. The flow of water from these three pipes was very small, hence suited to this technique. A five gallon bucket, calibrated in liters was used to capture the water. In three different trials, a stop-watch was used to time the filling of the bucket. The flow rate was calculated by:

$$Q(L/s) = V(L)/t(s)$$

The influents from the fourth pipe at pond 18, and pond 9 were determined using the Manning Equation. The Manning equation is used to calculate flow rates for uniform steady flow in open channels in which the top surface of the water is exposed to the atmosphere (Mott, 1990). The equation for the volumetric flow rate is as follows:

$$Q(m^3/s) = (1.00/\eta) \, A \, R^{2/3} \, S^{1/2}$$

Where $\eta$ is the dimensionless resistance factor dependent on the channel surface, R is the hydraulic radius in meters, A is the cross-sectional area for flow in square meters, and S is the dimensionless channel slope. Pipe dimensions and channel slopes were measured using a measuring tape.
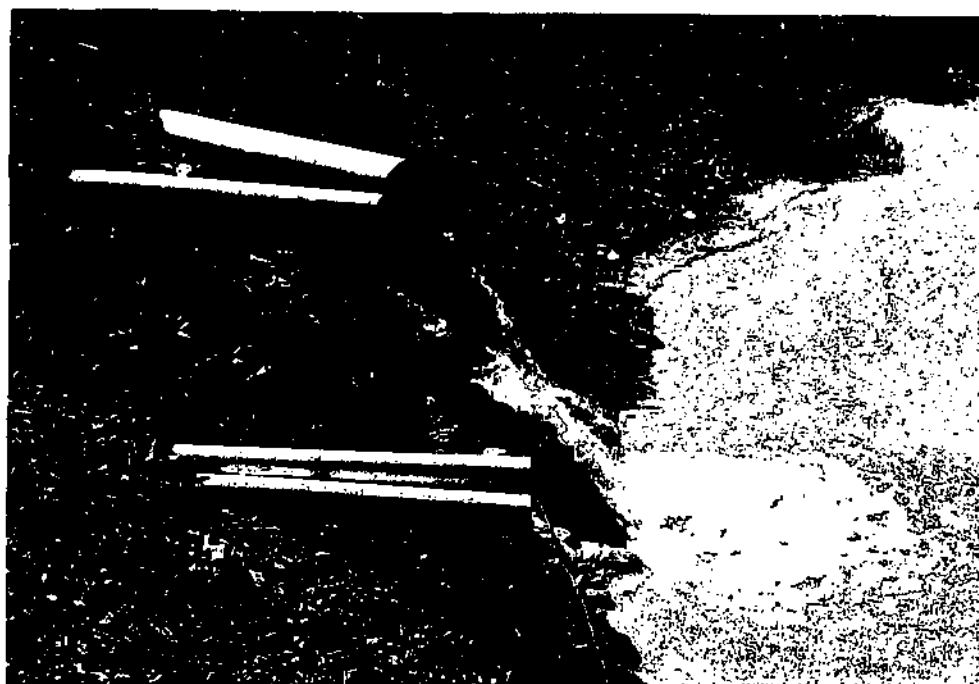
Figure 3.2. Drainage into pond 18 consisting of four pipes.

## 3.3 Surface Water Sampling

Surface waters were collected from the adit, pond seeps, geothermal vents, and the above specified ponds. Sub-surface waters were collected from ponds 5, 9, and 11 only. The water in pond 18 was only 6 inches deep, hence it was assumed that the difference between surface and sub-surface waters would be insignificant. The sampling sites were located as close as possible to the point of discharge, where it was assumed the water was well mixed. In all cases, four aliquots were taken at each sampling site; three in 1-L polyethylene containers, and one in a 1-L glass jar. Preservation techniques and sample containers were based on the type of analysis to be performed on each sample aliquot. Table 3.1 summarizes the containers and preservation techniques used for each aliquot.

Table 3.1: Sample containers and preservation techniques.

| ALIQUOT | ANALYSIS TO BE PERFORMED | SAMPLE CONTAINER | PRESERVATION TECHNIQUE |
|---------|--------------------------|------------------|------------------------|
| 1 | TOC[a], TSS[b], TDS[c] | 1-L glass jar | Unfiltered Cooled to 4 °C |
| 2 | Total metals | 1-L polyethylene jar | Unfiltered Acidified[d] Cooled to 4 °C |
| 3 | Dissolved metals | 1-L polyethylene jar | Filtered Acidified[d] Cooled to 4 °C |
| 4 | Anions | 1-L polyethylene jar | Filtered[e] Cooled to 4 °C |

[a] Total organic carbon; [b] Total suspended solids; [c] Total dissolved solids;
[d] Concentrated $HNO_3$ to pH < 2; [e] 0.45 μm membrane.

### 3.3.1 Surface Water Sampling Method And Equipment

Unfiltered surface water samples were collected as grab samples from the surface at each location. Filtered samples were collected using a 0.45 micron in-line filter, and a peristaltic pump. A Geotech dispos-a-filter (#GD 045700) was inserted in a line of 1/8" x 1/8 " Tygon laboratory tubing (formulation R1000). This assembly was then attached to a MasterFlex electric peristaltic pump (Model # 7520-00), with a #7017-21 pump head. The entire set-up was powered by an 8000 watt Sears Craftsman portable generator. All sub-surface water samples were collected using the pump assembly; unfiltered samples without the in-line filter. Pump lines, filters, and sample bottles were thoroughly rinsed with the water to be sampled prior to the actual sampling event.

To ensure that the sub-surface samples were taken at the liquid-solid interface, a six foot plastic dowel was attached to 2' x 2' plastic base. The end of the Tygon tubing was then attached to the bottom of the dowel at the base using hose clamps, and the apparatus was placed on the sediment surface. This apparatus served a dual purpose, as the water level could be marked on the dowel and thus the water depth determined.

Sampling containers and equipment were cleaned according to specified operating procedures described in EPA Publication SW-846, Test Methods for Evaluating Solid Waste, Volume 1.

### 3.3.2 Surface Water Sample Analysis

Field parameters, such as temperature, pH, redox potential (Eh)[5], specific conductance, and dissolved oxygen (DO) were measured prior to sampling. The

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[5]Problems with the Orion Redox Electrode (Model 96-78), both the original and the back-up, were encountered when attempts were made to determine the relative millivolts. Therefore, this parameter was omitted from the analysis.

temperature and pH were determined using an Orion Model 250 Meter. A two point calibration, using buffer solutions with pHs of 4.01 and 7.00 s.u. was performed before the pH was measured. The specific conductance was measured using an Orion Model 122 Meter and an Orion 012210 conductivity cell. Readings from the conductance meter were verified in the field using OakTon standard solution, Lot # 5-0110 with a specific conductance of 1413 μS. The DO was measured using an Orion Model 820 Dissolved Oxygen Meter with the Orion probe Catalog No. 082010.

Other field parameters, such as $Fe^{2+}$ and alkalinity were determined during or immediately after the sampling event. $Fe^{2+}$, when measured, was determined colorimetrically using CHEMetrics' CHEMet ampule kit #K-6010. The method for quantifying results was a visual color comparison with comparator standards. Alkalinity was determined using the Hach Method 8221 from the Hach Water Analysis Handbook. This is a buret titration using Hach standard 0.16N or 0.02N $H_2SO_4$. Since all samples had pHs of less than approximately 8.3, only bicarbonate alkalinity was determined. All samples were titrated to an end point of pH 4.8 using the Hach Digital Titrator model 16900-01.

Laboratory analysis was performed to determine total metals, dissolved metals, total suspended solids (TSS), total dissolved solids (TDS), and sulfate ($SO_4^{2-}$) and chloride (Cl-) anions. A 27 metal ICP spectroscopic analysis (EPA Method 3010A/6010) was initially performed on the adit and pond 5 surface water samples in order to determine the primary contaminants to be analyzed in the remaining samples. Subsequent analysis was performed on the same samples for silver, arsenic, cadmium, and lead by Graphite Furnace Atomic Absorption (Methods 3020/7761, 7060, 7131, and 7421, respectively); and for mercury by Cold Vapor Atomic Absorption (Method 245.1/7470) because of the need for lower detection limits[6]. Results of the initial scans have been provided in the

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[6]Initial ICP, GFAA, and CVAA analysis was performed by Analytica Environmental Laboratories, Inc. Broomfield, CO 80021.

Appendix. From these results, the primary metal contaminants were targeted for analysis in the remaining samples[7]. Table 3.2 provides a summary of analysis performed on the remaining samples.

Table 3.2: Laboratory analysis of water samples.

| ANALYSIS | ANALYTE | METHOD (digestion/analysis) |
|---|---|---|
| Total metals by ICP | Ca, Cu, Fe, Mg, Mn, Zn, K, Na | EPA 3010A/6010 |
| Dissolved metals by ICP | Ca, Cu, Fe, Mg, Mn, Zn | EPA 200.7/3020 |
| Total and Dissolved metals | Cd | EPA 3020A/3020 |
| by GFAA | Pb | EPA 3020A/7421 |
| Anions by | | |
| Ion Chromatograph | $SO_4^{2-}$ | EPA 300.0 |
| Auto colormetrics | $Cl^-$ | EPA 325.2 |
| TDS | TDS | EPA 160.1 |
| TSS | TSS | EPA 160.3 |

## 3.4 Sediment Sampling

Sediment samples were collected from ponds 5, 9, 11, and 18 at the same location in the ponds where the water samples were taken. In order to determine the nature and composition of the sediment throughout the lifetime of the ponds, it was necessary to sample the entire depth of the ponds. This was accomplished by extracting core samples from three of the four specified locations, and then segmenting the cores based on visual stratification. Pond 5 sediments were collected as a grab sample since there was not

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[7]Analysis not performed by Analytica Environmental Laboratories was performed by Accu-Labs Research, Inc. Golden, CO 80403.

enough sediment to core. Grab samples where collected using a 5 gallon bucket to scoop the sediment up.

### 3.4.1 Sediment Sampling Method

Core samples were collected in 4 inch diameter PVC tubes, from ponds 9, 11, and 18. The samples were collected by placing a tube, fitted with a piston, securely into a collar designed with protruding handles (Figure 3.3). The piston was secured to a cable issuing from a reel and winch mounted on a raft constructed with a moonhole. The bottom of the tube was placed on the surface of the sediment inside the moonhole, and the base of the piston was positioned at the water surface. Using the winch, the cable attached to the piston was then pulled taut without disturbing the piston position. The tube was manually pushed into the sediment using the collar handles, causing the piston to move up the tube yet remain at the water surface. The action of the piston created a vacuum within the tube, stabilizing the cored sample as it was being extracted. Extraction was completed by wrapping the cable around the collar handles and pulling the entire assembly out using the winch. An end cap was fastened to the bottom of the tube as soon as it was accessible.

The cores ranged from 40 to 242 centimeters in length, and a rack was designed to hold the core upright during segmentation. Each core was visually inspected for stratification, and sampling intervals were determined based on the stratified configuration. Samples were extruded out of the top of the core by inserting a second piston in the bottom, and using a hydraulic jack to physically pump the samples out (Figure 3.4). Each predetermined interval was gauged with pre-cut 4 inch PVC rings calibrated in centimeters. Gallon sized baggies were placed over the top of core during extrusion to catch the samples, and minimize exposure to oxidizing conditions. Samples that were too

soupy were attained using turkey basters. The samples were immediately cooled to 4°C for preservation.

### 3.4.2 Sediment Sampling Equipment

The equipment used to perform the coring and segmenting was designed and built by Ron Miner and Randy Miner, Research Technicians in the Department of Chemical Engineering and Petroleum Refining at the Colorado School of Mines. The coring tubes, pistons and collar were provided by Dr. Charles Holmes, a geochemist of the U.S. Geological Survey.

The raft was 10' x 10' square with a 3' x 3' square moonhole directly in the center. A quadripod, extending from each corner of the base to the center, was attached to support the cores and cable and winch assembly. The base of the raft was constructed of 3/4 " standard expanded metal grating and edged with 1/8" thick 2-inch angle iron. The quadripod was made of 14-gauge, 1½" square tubing. A 1/8" aircraft cable winch from Dutton-Laison Co. (Model #DL1402) was attached to one leg of the quadripod, and a reel was mounted on the top. Eight 25-gallon metal barrels were used to keep the entire apparatus afloat (Figure 3.5).

The rack used to hold the cores during extrusion was 10-feet high, and built of 4-inch channel iron. It was held to a van with C-clamps, and the cores were held to the rack with 3, 4-inch. galvanized metal conduit clamps (Figure 3.6). A 20-inch tall, 4-ton hydraulic jack (Model #H68475) with a 14-inch throw was used to push the sediment up. Twelve inch extensions were made with ½" steel pipes, threaded on each end and attached with ½" couplings. Sample collection was performed from the top of the van. The coring tubes ranged from 4-10 feet in length, and the pistons and collar were fashioned to tightly fit the tubes.

Figure 3.3. Core sampling apparatus with the piston and collar.
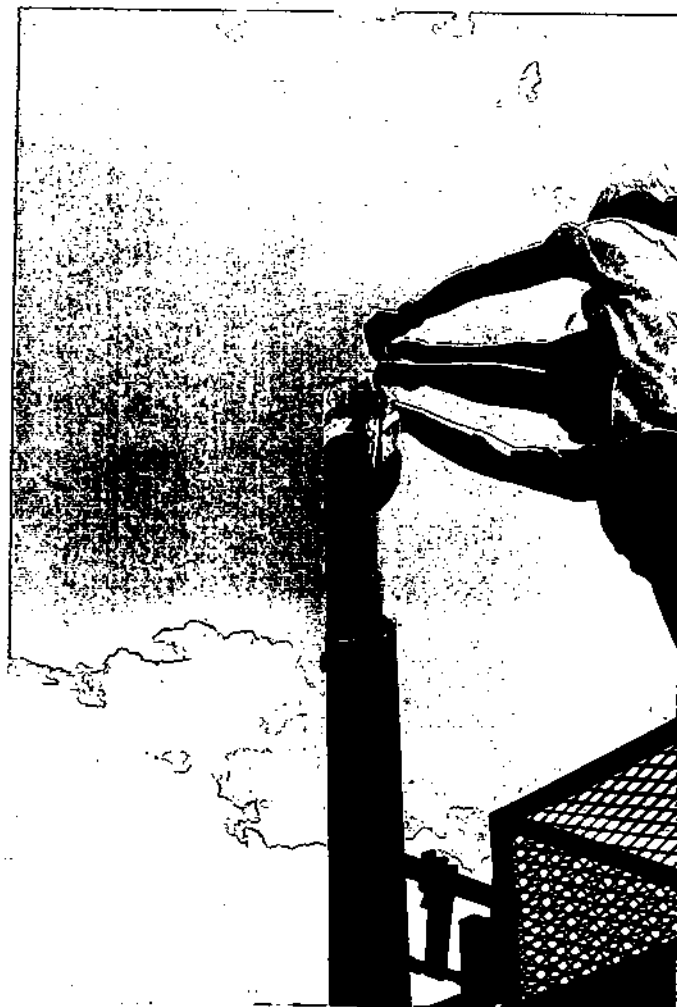
Figure 3.4. Sampling from the top of the core.
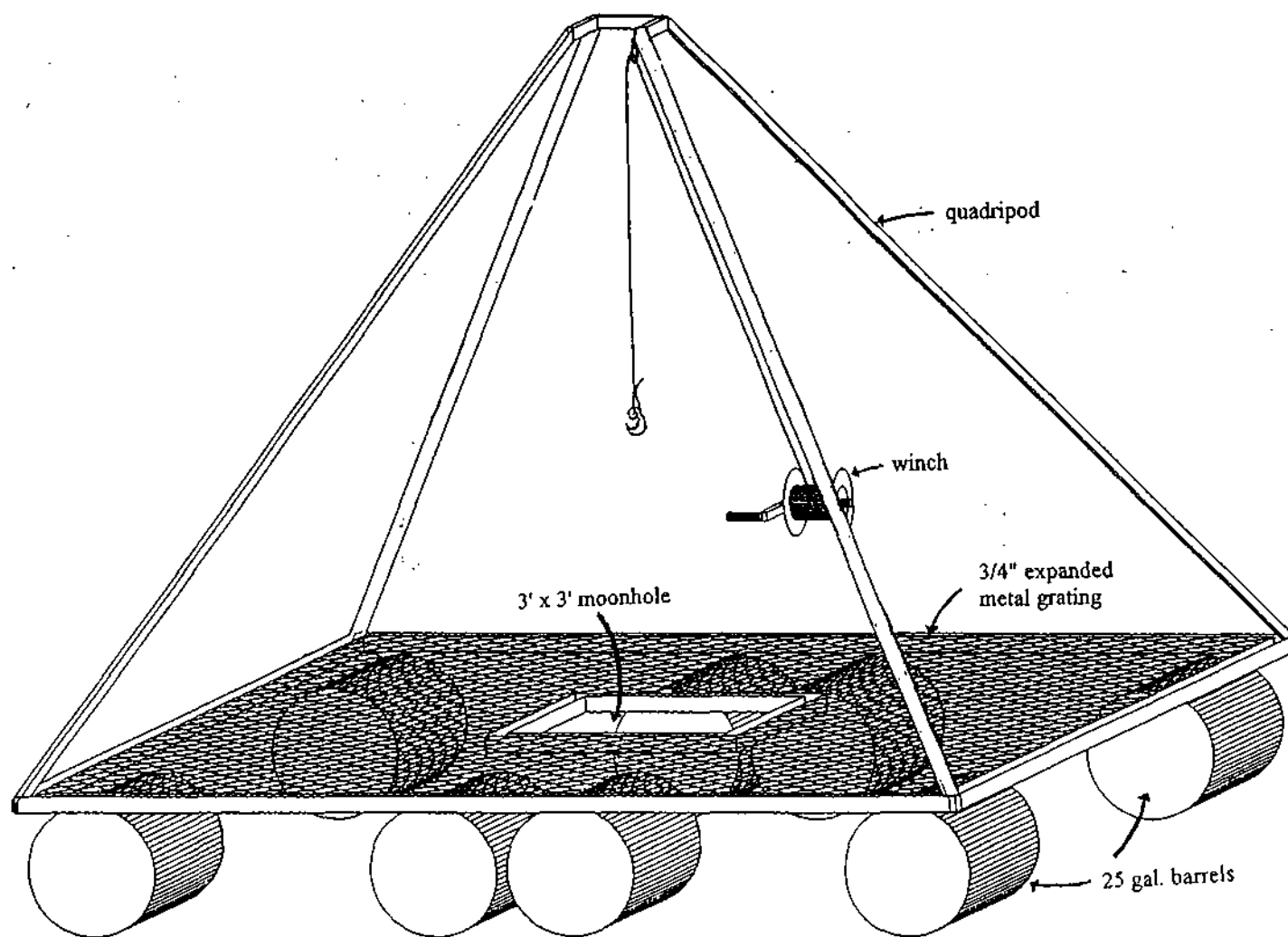
Figure 3.5. Custom built raft used for coring. Designed by research technicians in the Department of Chemical Engineering and Petroleum Refining at the Colorado School of Mines.

Labels in figure: quadripod, winch, 3/4" expanded metal grating, 3' x 3' moonhole, 25 gal. barrels

Figure 3.6. Rack designed to hold the core upright during segmentation.

### 3.4.3 Sediment Sample Analysis

Chemical and physical analysis for sediments collected included visual descriptions .of each segment, and determination of water content and total metal concentrations. Visual descriptions, performed in the field, consisted of the general consistency, color, and odor. Water content was determined for the two longest cores from ponds 11 and 18, in order to assess the storage capacity and lifetime of the pond system. The samples were analyzed for total metals to ascertain the fate of metals transported into the system.

Water content determinations were performed at the laboratories in the Department of Chemical Engineering, using a BLUE M oven (Model #OV-475A-3), a Sartorius analytical scale (Model #1712MP8), and a PYREX brand desiccator. Ceramic crucibles were brought to constant weight (in grams to 3 decimal places), in a 250°C oven. Samples were then pre-weighed, heated in a 75°C oven, and cooled in a desiccator. This process was repeated until the crucibles and samples were at constant weight. The lower temperature used to dry the samples was used to ensure that only free water was being driven off.

Total Ca, Cu, Fe, Mg, Mn, Zn, K, and Na were determined using ICP spectroscopic analysis (EPA Method 3050A/6010). This analysis was initially performed on the top, middle, and bottom segments of each core in order to determine the relative homogeneity of the columns. The consequences of the initial analysis dictated whether further inspection was necessary. For those cores whose samples resulted in metal concentrations of the same order of magnitude, homogeneity was assumed, and no further samples were analyzed. Conversely, cores whose samples exhibited varying orders of magnitude merited further analysis. Cores from ponds 9 and 11 were considered homogenous. The core from pond 18 required additional sampling throughout the column. Pond 5 was a grab sample, and only one sample was analyzed. Results of the analysis have been provided in the Appendix.

## 3.5  Pore-water Sampling

Pore-water samples were collected from all sediment samples.  In most cases, two aliquots were taken at each sampling site; both in 60-ml polyethylene containers.  Where inadequate samples were available, the single aliquot was collected and the type of analysis to be performed was alternated throughout the core.  Metals analysis was always considered a priority.  Preservation techniques were based on the type of analysis to be performed on each sample aliquot.  Samples to be analyzed for dissolved metals were preserved with concentrated $HNO_3$ to a pH < 2 and cooled to 4°C.  Samples to be analyzed for the anions $SO_4^{2-}$ and $Cl^-$, and TDS were cooled to 4°C.

## 3.5.1  Pore-water Sampling Method

Pore-waters were extracted from the sediment samples by placing the sediment in Fisher brand 50 ml polypropylene centrifuge tubes with caps (#14-375-150), and then centrifuging in a constant speed IEC Clinical Centrifuge, 7100 rpm/5125 G (IEC# 428).  Each batch was centrifuged for 15 minutes, and the water drawn off for filtration.  A 47 mm Millipore microfiltration vacuum assembly with 0.45 μm Millipore filters (#04700), was used to filter the samples.  A clean 50 ml centrifuge tube was placed in the top of the 1-L catch flask; where the lip of the tube prevented it from falling all the way through.  A fritted glass support base, attached to a 300 ml glass funnel with an aluminum clamp fit perfectly over the flask and tube.  Suction was applied to the apparatus using an aspirator adapted to a faucet.  The entire ensemble was cleaned between samples with 5% $HNO_3$, and rinsed thoroughly with distilled water.  Sediment samples which appeared anoxic (black, or sulfur smelling) were dealt with in a nitrogen atmosphere using a LabConCo glove box.

## 3.5.2 Pore-water Sample Analysis

Field parameters such as, temperature, pH, specific conductance, and dissolved oxygen (DO) were measured prior to filtering the sample. The temperature, and pH were determined using an Orion Model 250 Meter. A two point calibration, using buffers with pHs of 4.01 and 7.00 s.u. was performed before the pH was measured. The specific conductance was measured using and Orion Model 122 Meter and an Orion 012210 conductivity cell. Readings from the conductance meter were verified in the field using OakTon standard solution, Lot # 5-0110 with a specific conductance of 1413 µS. The DO was measured using an Orion Model 820 Dissolved Oxygen Meter with the Orion probe Catalog No. 082010.

Other field parameters, such as $Fe^{2-}$ and alkalinity were also determined prior to filtering however, only samples that produced adequate amounts of water were tested. $Fe^{2+}$, when measured, was determined colorimetrically using CHEMetrics' CHEMet ampoule kit #K-6010. The method for quantifying results was a visual color comparison with comparator standards. Alkalinity was determined using the Hach Method 8221 from the Hach Water Analysis Handbook. This is a buret titration using Hach standard 0.16N or 0.02N $H_2SO_4$. A micro titration technique was developed to conserve sample. All samples were titrated to an end point of pH 4.8 using the Hach Digital Titrator model 16900-01.

Laboratory analysis was performed to determine dissolved metals, total dissolved solids (TDS), and sulfate ($SO_4^{2-}$) and chloride (Cl-) anions. However, due to the small sample sizes, metal and anion analysis were alternated. Dissolved Ca, Cu, Fe, Mg, Mn, Zn, K, and Na were determined using ICP spectroscopic analysis (EPA Method 3010A/6010). This analysis and TDS (EPA Method 160.1) were performed on samples corresponding with sediment samples analyzed. Sulfate and chloride anions (Methods

300.0 and 325.2, respectively were tested for in alternating samples. The results of these analysis, as well as a description of which samples were analyzed within the core has been provided in the Appendix.

Chapter 4

## DISCUSSION OF RESULTS

### 4.1 Introduction

The basic goal of this section is to present and evaluate existing environmental conditions at the St. Louis pond site, and to attempt to identify the sources and fates of the constituents under investigation. In addition, an engineering approach to the analysis of the site will be performed. This analysis provides the necessary design parameters needed to propose hypothetical processes for the treatment of the drainage. The presentation of these processes will be a first approximation of the application of the particular technology to this site, and should not be considered a final design. Finally, performance of the software programs investigated for modeling the drainage and subsequent treatment will be discussed. Only a condensed summary of pertinent data is given in this section. The complete results of the sample analysis and all the historical data gathered can be found in the Appendix.

The field work conducted as a part of this study included measuring flow rates and sampling surface waters and pond sludge at various locations. These locations have been provided in Figure 1.2. The results and subsequent evaluation of the measurements and sample analysis are described in the following sections.

## 4.2 Flow rate and Water Loss Analysis

The determination of the location of flow rate measurements was motivated by the observation of overflow of drainage from a hyplon-lined channel carrying water from the treatment plant to pond 18, the evidence of possible seeps west of pond 18 (Figure 3.1), and the existence of geothermal springs in ponds 5 and 6. Since flow rates at these locations are not easily measured, three control volumes were established and flow rates into and out-of these volumes were determined. This facilitated the use of the following material balance for calculating the unknown flow rates:

$$d(\rho V)/dt = m_i - m_o - m_u$$

Where $\rho$ is the drainage density, and is assumed constant, V is the volume of water in the control volume at time t, $m_i$ is the rate of mass into the system, $m_o$ is the rate of mass out of the system, and $m_u$ is the rate of unknown mass lost from the system.

Assuming the system is at steady state (ie. no accumulation of water), and dividing by the constant density, the resulting equation simply becomes the difference between input and output volumetric flow rates in gallons per minute (gpm):

$$V_{unknown} = V_{input} - V_{output}$$

The control volumes selected for this analysis were:

1. The lime treatment plant and hyplon-lined channel, with the adit flow ($V_{input}$) and the influent to pond 18 ($V_{output}$) as input and output, respectively. The unknown flow rate ($V_{unknown}$) is the overflow from the hyplon-lined channel.

2. Ponds 11 through 18, with the influent to pond 18 and the influent to pond 9 as input and output, respectively. The unknown flow rate in this case is the possible seeps west of pond 18.

3. Ponds 5 through 9, with the influent to pond 9 and the CPDES outfall as input and output, respectively. The unknown flow rate is the geothermal springs in ponds 5 and 6.

Table 4.1 provides the measured flow rates with their associated experimental error, in addition to the results of the material balances.

Table 4.1: Flow rate measurements at the St. Louis site.

| Location | Flow rate, gpm[a] | Experimental error |
|---|---|---|
| Adit effluent | 2200 | 5% |
| pond 18 influent | 1600 | 2% |
| pond 9 influent | 1200 | 51% |
| CPDES outfall | 1400 | 8% |
| Channel overflow | 600 | |
| Pond 18 seep | 400 | |
| Geothermal springs | -200[b] | |

[a]gallons per minute
[b]The negative value for this flow rate indicates an input to the control volume.
Note: The uncertainty of these values are the result of the propagation of systematic errors due to experimental measurements.

The material balances performed for each control volume has provided an estimate of the flow rates of the channel overflow, pond 18 seep, and the geothermal springs. However, the experimental error of 51% associated with the pond 9 effluent renders the seep and geothermal spring flow rates questionable. This high error was due to the nature

of the flow from pond 11 to pond 9. The water flows through a culvert between the two ponds, and the location of the inlet in pond 11 was unknown because it was below the surface of very murky water. Hence, a rough estimate of the distance of the flow had to be made resulting in a flow rate that could be as high as 1800 gpm and as low as 600 gpm. The overflow from the hyplon-lined channel is less questionable, since fairly accurate measurements of the adit and pond 18 flow rates were attained.

The most significant observation to be made in these results is the 40% difference in the adit and outfall flow rates. Although this difference has been accounted for through visible losses due to overflow and seepage, less obvious transport paths need to be considered such as infiltration and evaporation. Infiltration through the bottom of the ponds directly into groundwater could be considerable, since the ponds have been constructed with unconsolidated material and are located within an alluvial aquifer[8]. However, this flow rate is not measurable.

Evaporation losses, although not easily determined, can be estimated by assuming only convective mass transfer is occurring at the air-water interface through a turbulent boundary layer created by wind blowing across the pond surfaces. The general equation for convective mass transfer is:

$$m_w = k_c A(C_{w1} - C_{w2})$$

Where $m_w$ is the flux of water leaving the pond surface through the boundary layer in kmol/s, $C_{w1}$ is the concentration of the water in the air at the surface in kmol/m$^3$, $C_{w2}$ is the concentration of water in the air flowing across the pond, A is the surface area available for mass transfer in m$^2$, and $k_c$ is the convective mass transfer coefficient in m/s. Assuming that the local humidity is zero (ie. there is no water in the air blowing over the

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[8] An alluvial aquifer is defined as water bearing sediment deposited by a river in a flood plain.

ponds, so $C_{W2} = 0$), and that the water vapor in the air at the surface of the ponds is ideal, a conservative estimate is given by:

$$m_W = k_c A(P_{vap}/RT)$$

Where $P_{vap}$ is the vapor pressure of water at the surface of the pond in Pascals and dependent on the temperature of the water in the ponds, R is the ideal gas constant given as 8314 Pa/Kmol K, and T is the temperature of the water in degrees Kelvin.

Assuming that the wind blowing across the pond surface simulates flow parallel to a flat plate, a correlation for the convective mass transfer coefficient, $k_c$, in m/s, is estimated by (Geankoplis 1983):

$$k_c = 0.036 \; v \; Re^{-0.2} \; Sc^{-2/3}$$

Re is the dimensionless Reynolds number given by $Lv\rho/\mu$, L is the length of the pond in the direction of flow in meters, v is the velocity of the wind in m/s, $\rho$ is the density of air in Kg/m$^3$, and $\mu$ is the viscosity of air in Kg/m s. The Reynolds number is a measure of the turbulence of the air flowing past the pond surface and is determined by the ratio of kinetic forces ($\rho v^2$) to viscous forces ($\mu v/L$) in the air stream.

Sc is the dimensionless Schmidt number given by $\mu/\rho D_{ab}$, and $\mu$ and $\rho$ are the viscosity in Kg/m s, and density in Kg/m$^3$ of air, respectively. $D_{ab}$ is the mass diffusivity of water in air in m$^2$/s, and is a measure of the movement of individual water molecules through air molecules by means of a concentration gradient. The Schmidt number is the ratio of the molecular diffusivity due to the movement of molecules ($\mu/\rho$) to the molecular diffusivity due to concentration gradients ($D_{ab}$), and it physically relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer. Table 4.2 lists the values used in determining the evaporation rates due to convective mass transfer.

Table 4.2: Numerical values and their sources used in the determination of the evaporation rate due to convective mass transfer.

| Parameter | Numerical value | Source |
|---|---|---|
| Wind Speed, v | 3.83 knots (1.97 m/s) | World Wide Web ftp://ftp.ncdc.noaa.gov/pub/data/ globalsod/august95.txt |
| Wind direction | North - South | ibid. |
| Length of flow, L | Varies from pond to pond | Figure 1.2 |
| Surface area, A | Varies from pond to pond | Figure 1.2 |
| Viscosity of air, $\mu$ | 1.98 $(10^{-5})$ Kg/m s | Perry and Chilton 1984 |
| Density of air, $\rho$ | 1 Kg/m$^3$ | Perry and Chilton 1984 |
| Diffusivity, $D_{ab}$ | 2.5 $(10^{-5})$ m$^2$/s | Perry and Chilton 1984 |
| Gas constant, R | 8314 Pa/Kmol K | Geankoplis 1983 |
| Vapor pressure, $p_{vap}$ | f(T), varied from pond to pond | Perry and Chilton 1984 |
| Temperatures, T | Temperature of each pond | Table 4.4, and assumptions for ponds not measured. |

In addition to convective mass transfer, evaporation also occurs due to solar radiation. The amount of solar energy required to evaporate one cubic centimeter of water is 597 calories (Davis and De Wiest 1966). The solar energy received at the earth's surface may average more than 700 calories a square centimeter per day ($cal/cm^2day$) in desert regions to less than 100 $cal/cm^2day$ in polar regions. Furthermore, water reflects about 10 percent of this energy (ibid.). Assuming that the Rico area receives 400 $cal/cm^2day$, the total energy available for evaporation is approximately 360 $cal/cm^2day$. Hence, the total evaporation can also be estimated from these approximations.

Table 4.3 provides the total surface area of each pond determined from Figure 1.2, and the estimated evaporation rates.

Table 4.3: Surface area and evaporation rates of each pond.

| Pond | N-S[a] length | E-W[b] width | Surface Area | Evaporation rate | |
|------|------|------|------|------|------|
| | ft | ft | ft$^2$ | convective gpm | radiative gpm |
| 18 | 350 | 200 | 70000 | 5 | 7 |
| 15 | 400 | 150 | 60000 | 4 | 6 |
| 14 | 150 | 150 | 22500 | 2 | 2 |
| 12 | 200 | 150 | 30000 | 2 | 3 |
| 11 | 150 | 150 | 22500 | 2 | 2 |
| 9 | 250 | 50 | 12500 | 1 | 1 |
| 8 | 100 | 250 | 25000 | 2 | 3 |
| 7 | 200 | 175 | 35000 | 3 | 6 |
| 6 | 150 | 200 | 30000 | 3 | 3 |
| 5 | 150 | 125 | 18750 | 2 | 2 |
| | | | Total gpm ==> | 26 | 35 |

[a]The north-south dimension.
[b]The east-west dimension.

The total evaporation due to both convective mass transfer and solar radiation is estimated to be approximately 61 gallons per minute. Although this rate is considerable, it still only represents 8 percent of the total loss of 800 gpm. In addition, the rate of accumulation of water in the sediment is only approximately 0.3% of the total loss. Hence, the majority of the loss is probably due to seeps and groundwater infiltration.

### 4.3 Water Quality Analysis

Water samples were taken throughout the pond system for the purpose of determining the efficiency of the lime treatment plant and associated settling ponds. Furthermore, samples were taken at the surface and at the solid-liquid interface to ascertain differences, if any, within the water column, and to detect possible redissolution of metals from the sludge. Samples were also taken from the geothermal springs located in ponds 5 and 6 to observe what effect they may be having on the chemistry of the water in these ponds. Finally, samples were drawn from a channel skirting the Dolores River west of pond 18 to confirm the presence of possible seepage.

A thorough analysis of the major constituents found in most natural waters was performed on all the samples, and can be found in the Appendix. The data presented here consists primarily of those constituents of concern in the CPDES permit (Table 2.1), and targeted for remediation. Iron and manganese, although not regulated, have been included because of their potential for adsorbing heavy metals. Alkalinity and sulfate ion concentrations have been included because of the dominant role they play in the chemistry of precipitation. Although silver is regulated on the CPDES permit, the initial scan performed on samples taken from the adit and pond 5 indicated that concentrations are below the detection limit of 0.0001 mg/L. Therefore, it was not measured in the

remaining samples. The results of the initial scan and the detection limits have been provided in the Appendix.

## 4.3.1 Adit and Pond Water Analysis

The analysis of total recoverable, dissolved, and suspended metals in the adit and pond waters have been presented together in a continuous line plot to facilitate a better understanding of the efficiency of the ponds as the water flows through the system. Suspended metal values were calculated as total recoverable minus dissolved metals. Figures 4.1, 4.2, 4.3, 4.4, 4.5, and 4.6 illustrate these values for cadmium, copper, zinc, lead, iron, and manganese, respectively. Furthermore, the values for both the surface waters (subscript a) and the interfacial waters (subscript b) have been displayed. Those metals regulated under the CPDES permit have also been compared to the 30-day average limits for the total recoverable metal. Table 4.4 list the other major constituents of concern in the same water including pH, alkalinity, total suspended and dissolved solids, and sulfate ion concentrations. The following discussion of metal concentrations is similar to observations made by Dr. Lorraine H. Filipek of Schafer & Associates in an unpublished report prepared for the Atlantic Richfield Company (Filipek 1995) on samples collected in May of 1995. A discussion of the efficiency of the treatment plant and ponds, as well as the effect the geothermal waters has on the system will be discussed in a later section after the sample analysis has been presented.

Cadmium, illustrated in Figure 4.1, exists mainly in the dissolved state in the adit drainage, and it appears that liming is successfully converting the dissolved metal to suspended metal through hydroxide precipitation. Approximately 80% of the total cadmium is removed in pond 18, as the concentration of this metal was reduced from 0.025 mg/L to 0.0058 mg/L. Only about 50% of the remaining cadmium is removed in

the rest of the pond system. The concentration at the CPDES out fall is 0.003 mg/L, and does not meet the permit limitation of 0.0004 mg/L. Cadmium is one of the more difficult metals to remove via hydroxide precipitation because it is extremely soluble relative to the other metal hydroxides, and its minimum solubility occurs at a pH of 11.2. The maximum pH observed in the pond system occurs in pond 18 with a pH of 8.33 directly after liming and gradually decreases to a pH of 7 at the outfall (Table 4.4). Hence, minimum dissolved concentrations are never met, and actually increase slightly by pond 5.

Copper, illustrated in Figure 4.2, exists mainly as suspended solids in the adit drainage. Unlike cadmium, copper's minimum solubility occurs at a pH of 8.8, and as the pH is increased to 8.33 through liming, 95% of the total copper is removed. By the time the water reaches pond 5, 98% of the total copper has been removed. The final concentration at the CPDES outfall of < 0.005 mg/L is well below the permit limitation of 0.024 mg/L.

Zinc, illustrated in Figure 4.3, exists primarily in dissolved form in the adit drainage, at a concentration of 4.3 mg/L. Through liming, the dissolved concentration is reduced dramatically, and by pond 11, 95% has been converted to a zinc hydroxide suspension and settled out. The remaining suspended and dissolved solid concentrations are constant throughout the pond system until pond 5, where the pH drops to 7 causing the zinc hydroxide suspension to redissolve. The final total zinc concentration of 0.3 mg/L exceeds the permit limitation of 0.237 mg/L.

Approximately 70% of the lead concentration, illustrated in Figure 4.4, is in a suspended state in the adit water. Similar to the other metals, most of the lead settles out in pond 18, and less than 0.005 mg/L of total lead remains in the water. This total concentration, which is well below the required permit limitation of 0.0099 mg/L remains constant throughout the pond system.

Iron and manganese are not regulated by the CPDES permit. However, according to Dr. Filipek, they play an important role in the adsorption of other heavy metals. The

Table 4.4: Analytical results of selected constituents for the adit and pond waters.

| Constituent | Adit | Pond 18 | Pond 11 | | Pond 9 | | Pond 5 | |
|---|---|---|---|---|---|---|---|---|
| | Surface | Surface | Surface | Interface | Surface | Interface | Surface | Interface |
| | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] |
| pH, s.u. | 6.29 | 8.33 | 8.13 | 8.12 | 8.18 | 7.92 | 6.91 | 6.93 |
| Alkalinity as $CaCO_3$ | 77 | 70 | 69 | 67 | 68 | 66 | 98 | 90 |
| TSS | 42 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| TDS | 820 | 820 | 860 | 840 | 830 | 840 | 890 | 880 |
| Sulfate | 420 | 350 | 530 | 550 | 310 | 310 | 570 | 510 |
| Temperature, C | 18.6 | 18.1 | 17.1 | 17.1 | 17.6 | 17.9 | 19.3 | 18.9 |
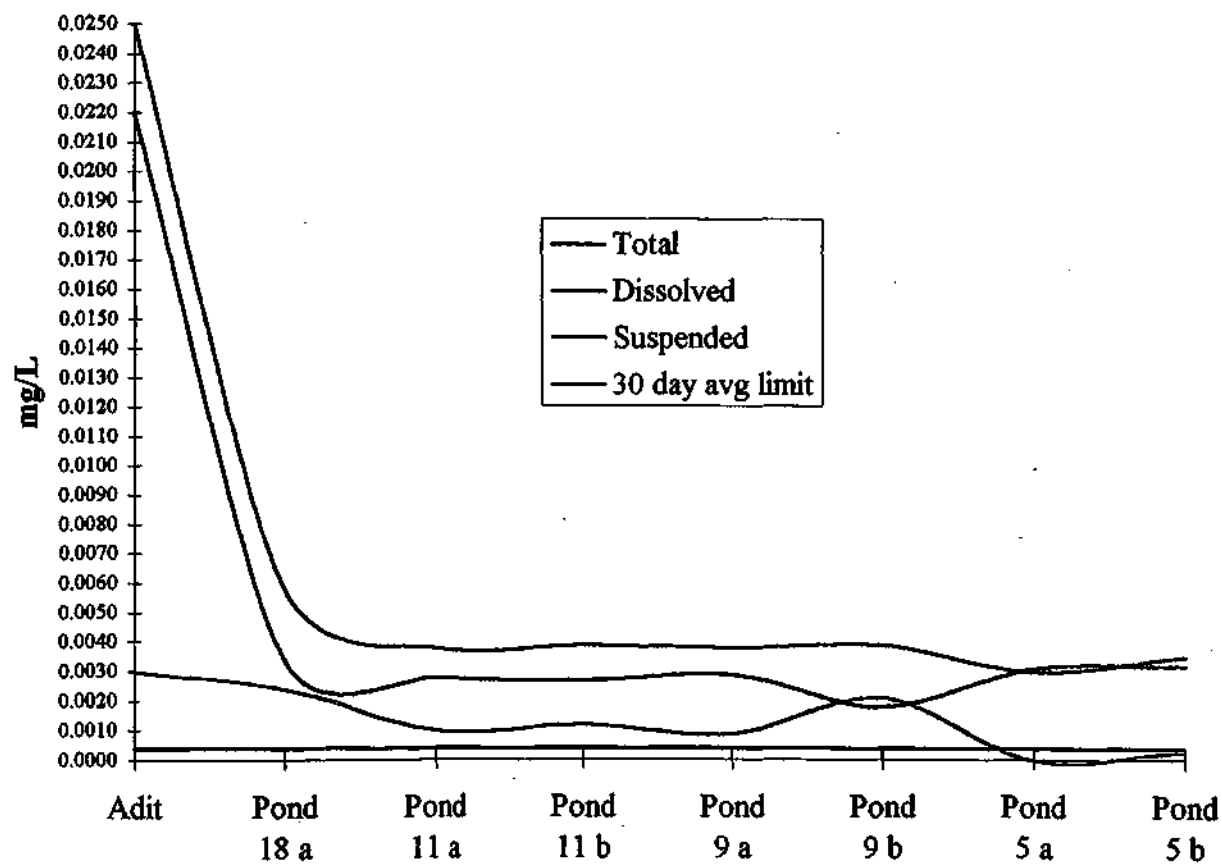
Figure 4.1: Cadmium concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are compared with the CPDES permit limitations.
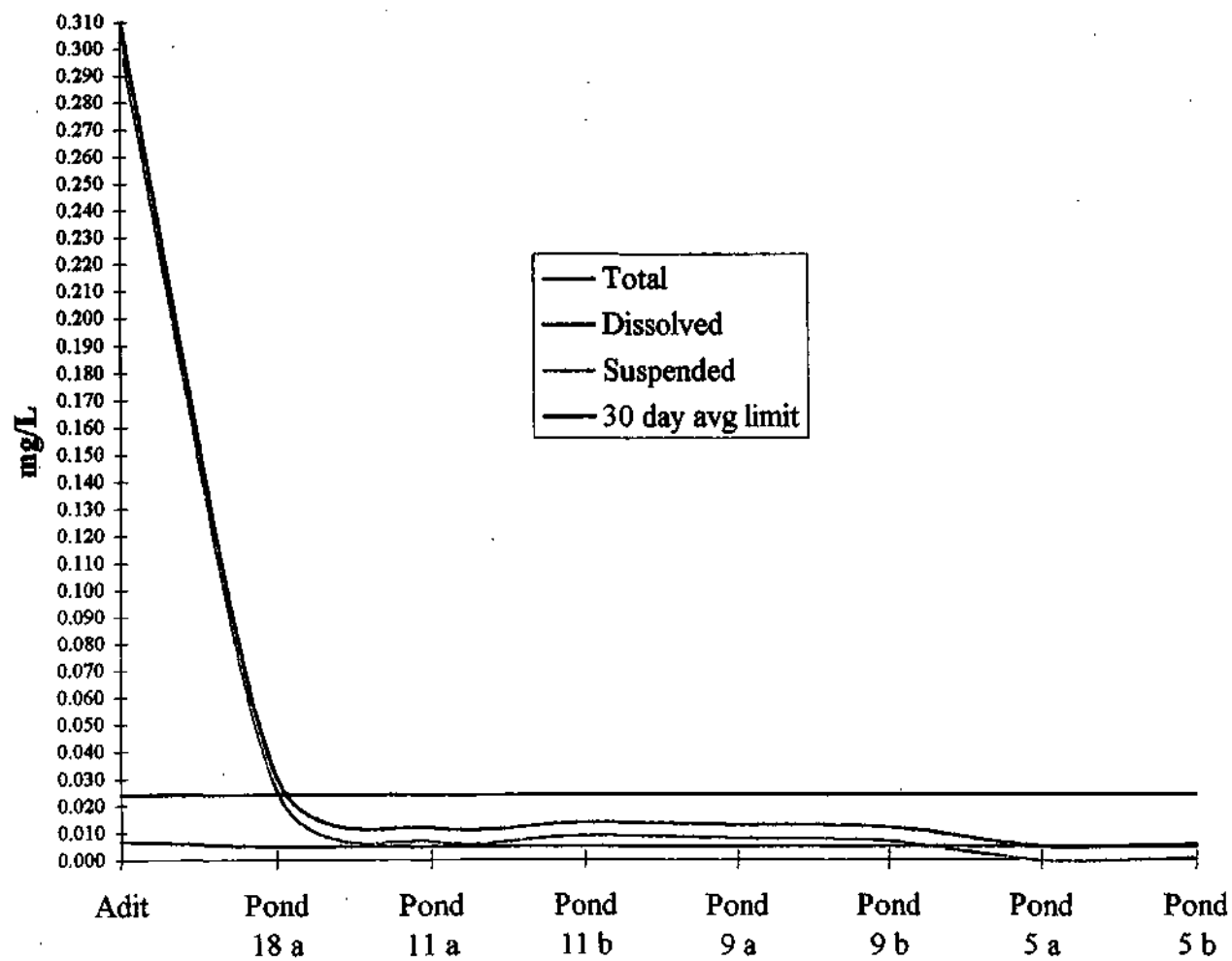
Figure 4.2: Copper concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are compared with the CPDES permit limitations.
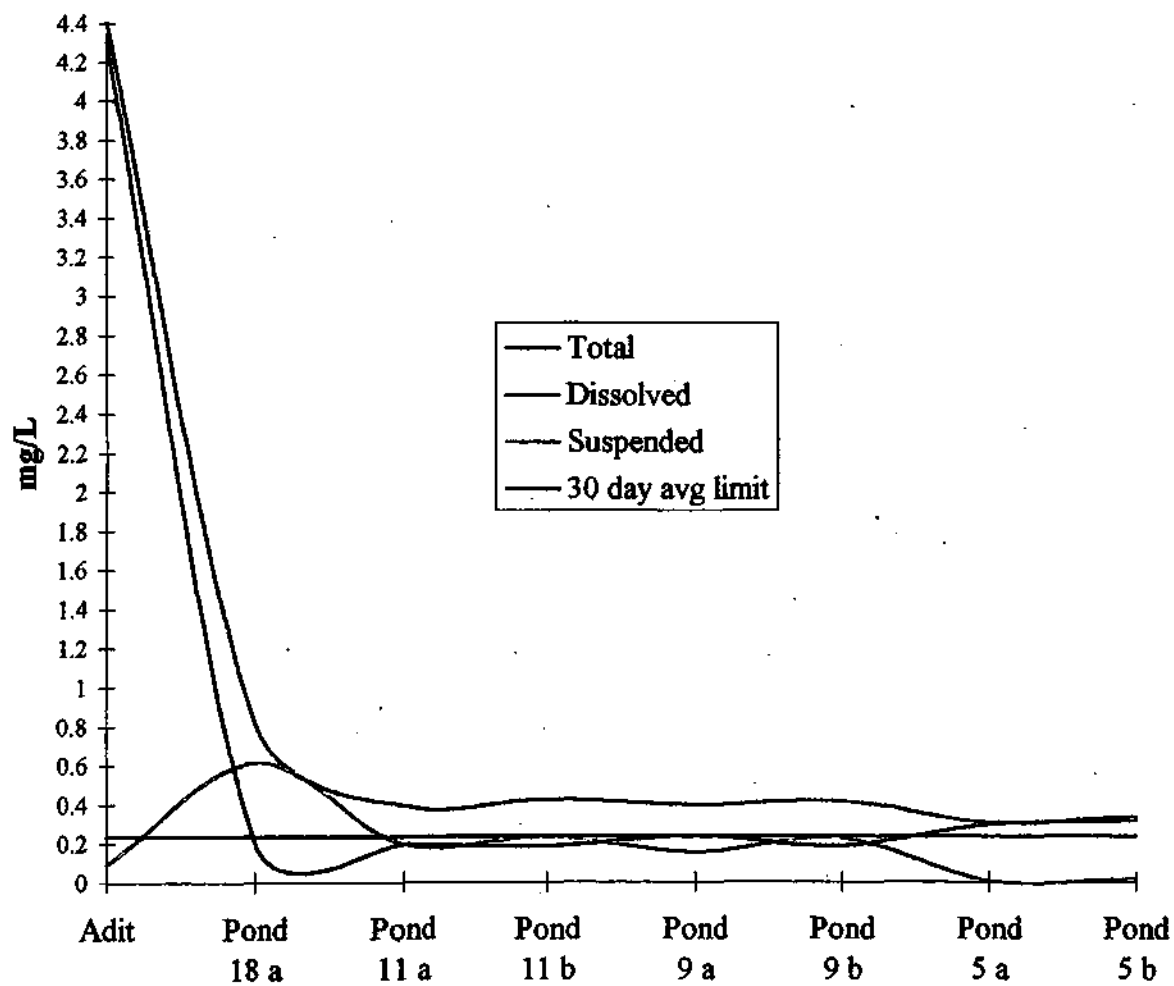
Figure 4.3: Zinc concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are compared with the CPDES permit limitations.
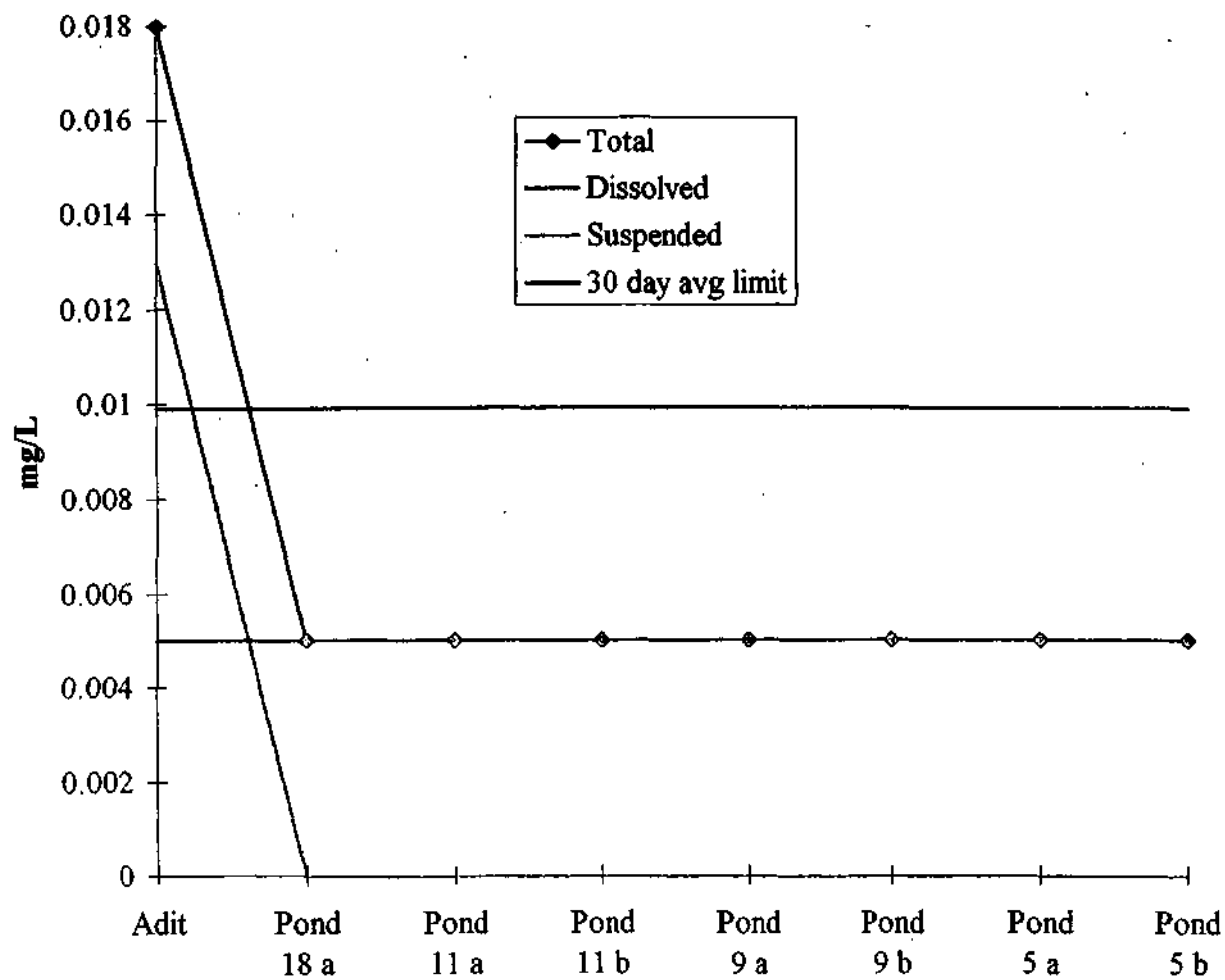
Figure 4.4: Lead concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are compared with the CPDES permit limitations.
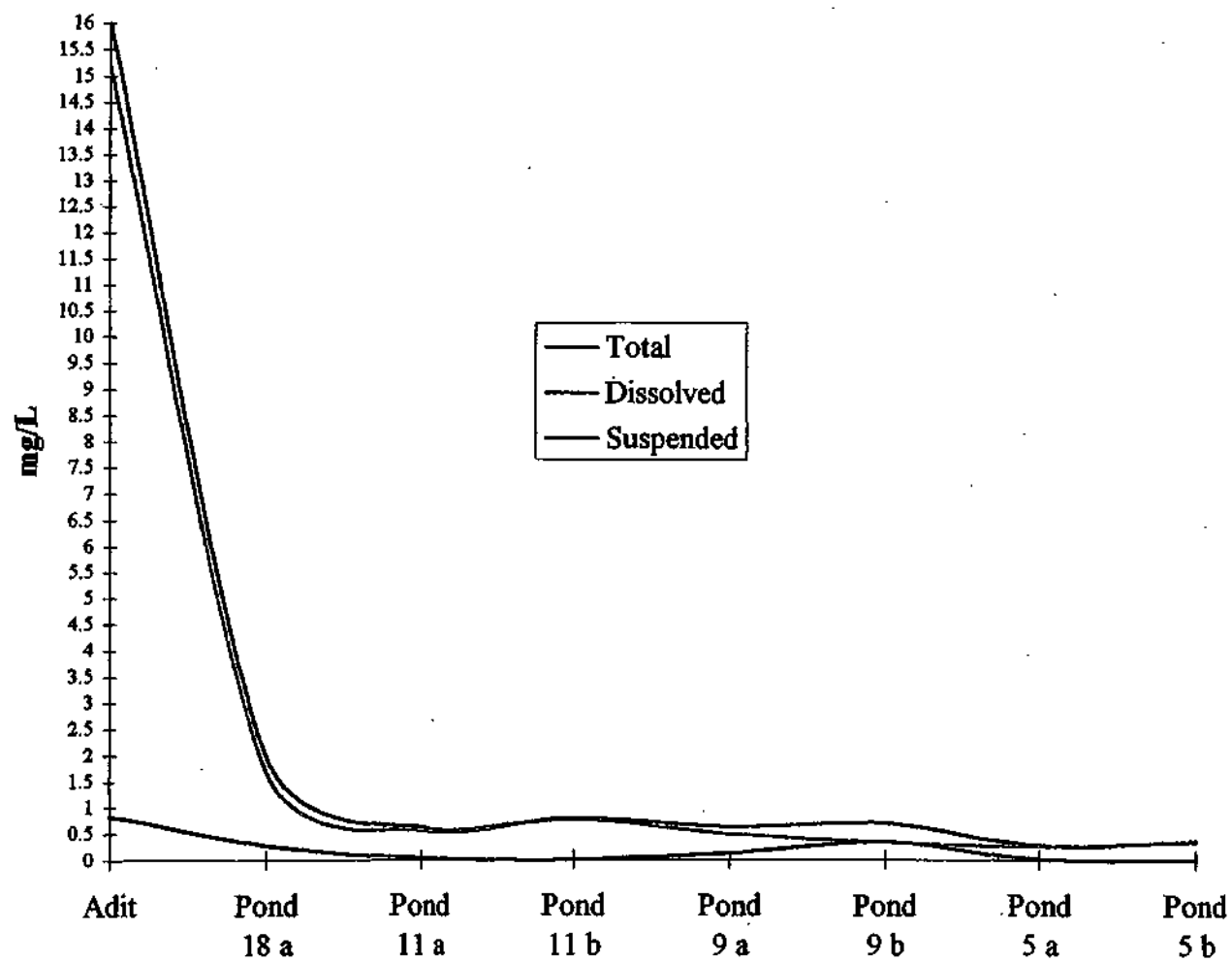
Figure 4.5: Iron concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are presented.
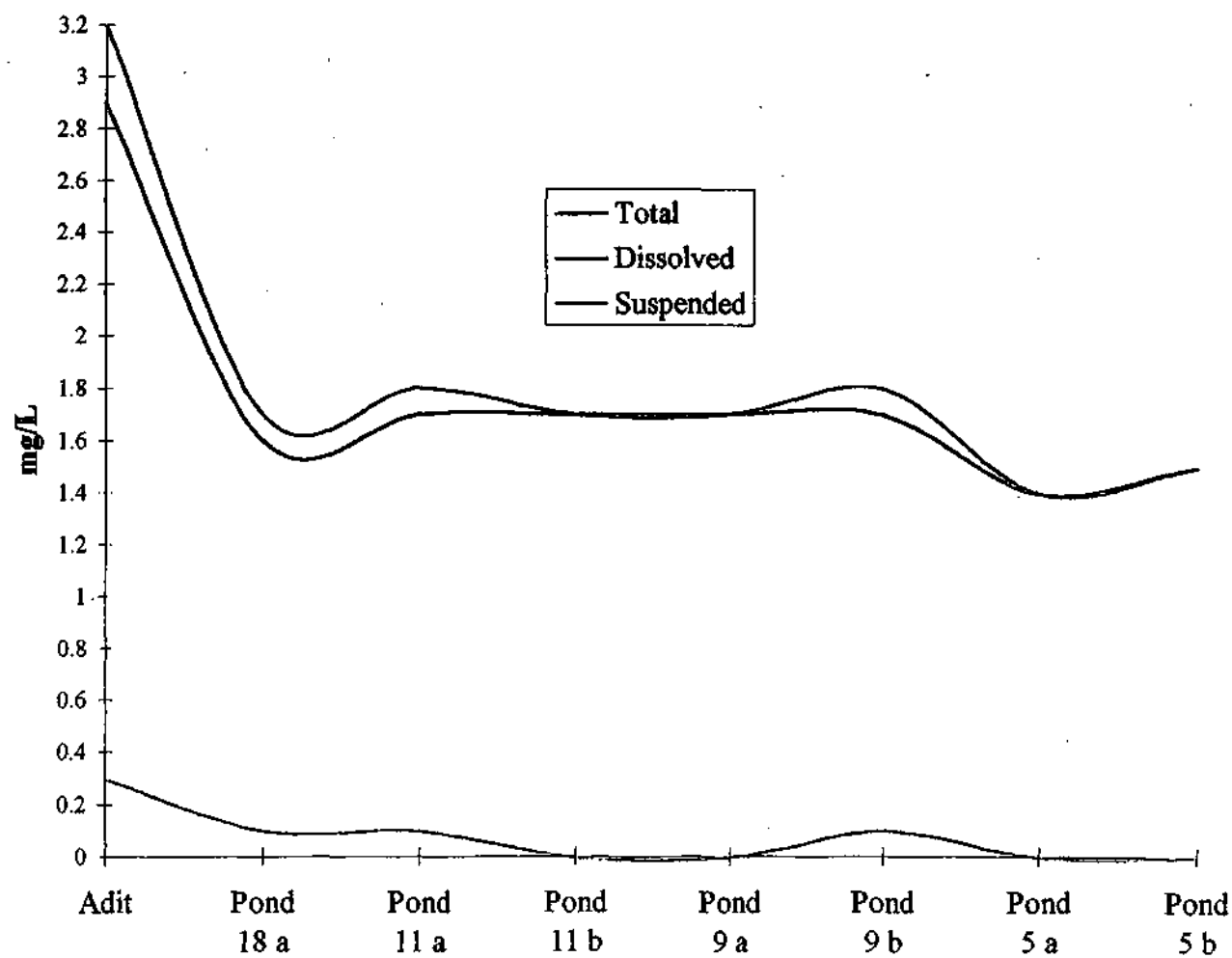
Figure 4.5: Manganese concentrations in the adit and pond water. The total recoverable, dissolved, and suspended concentrations in both the surface and interfacial samples are presented.

elevated concentrations of iron and manganese provide the necessary surface area to enhance coprecipitation. Hence, the total, dissolved, and suspended concentrations for iron and manganese are illustrated in Figures 4.5 and 4.6, respectively. Virtually all the iron in the adit sample exists as suspended solids, and by pond 11 approximately 96% has settled out resulting in a final concentration in pond 11 of about 0.7 mg/L. It is this iron hydroxide precipitate that gives the upper ponds their characteristic orange coloration, which is not observed in pond 5 through 9. Only 50% of the remaining suspended iron is removed in the lower ponds, resulting in a final concentration of 0.36 mg/L at the outfall. Dissolved concentrations are virtually non-existent at this point.

Contrary to iron, manganese is primarily in the dissolved form in the adit water. However, as the pH is increased to 8.33 through liming, approximately 50% of the manganese is converted to an insoluble hydroxide form and deposited in pond 18. The dissolved concentration of about 1.7 mg/L remains relatively constant throughout the ponds until the water reaches pond 5, at which point a slight decrease has been observed.

A comparison of surface and interfacial samples for each pond examined, indicates only subtle differences between the two. The most observable differences occurred in pond 9, and consisted primarily of an increase in suspended solids at the sediment interface. This could be due to a concentration gradient that develops as the metals settle. However, a more plausible reason for the differences is the sampling technique used. It was necessary to wade out into the pond to place the sampling apparatus at the bottom. This, more than likely disturbed the sediment causing an increase in the suspended metal concentrations.

### 4.3.2 Geothermal Springs and Pond Seeps

The results of the water analysis performed on the geothermal springs located near ponds 5 and 6 have been provided in Table 4.5. By comparing these results with pond 5 results, a general understanding of the effect the springs may have on water quality can be attained. The spring waters have extremely low concentrations of all the permitted metals (Cd, Cu, Pb, and Zn). However, dissolved concentrations of the same constituents in the pond 5 samples have increased while total concentration remained fairly constant. This is probably due to the fact that the spring water with a pH of about 6.5 is mixing with pond water with a pH of about 8, resulting in a lower pH at the outfall. Due to the amphoteric nature of metal hydroxides, a decrease in pH will cause the suspended material to redissolve. The exceptions to the above discussion are lead which was essential removed from the water in the upper ponds, and copper which displays an overall concentration reduction probably due to dilution by the spring water. In addition to the change in metals concentrations, alkalinity, TDS, and sulfate ion concentrations have increased in pond 5. The spring water concentrations of these constituents is considerable and has caused the pond 5 values to increase.

Finally, water samples were taken from a channel of the Dolores River west of the ponds to confirm possible seepage from the system. Results from the analysis can be found in Table 4.6. After examining the results of the analysis of samples taken upstream and downstream from the apparent seep, seepage from the ponds cannot be confirmed. Since the entire area is geothermally active, it is entirely possible that the presence of the orange iron hydroxide precipitate in this channel occurs due to seepage from additional geothermal springs. Several constituents in the analysis tend to confirm the source as geothermal springs such as an increase in temperature, a decrease in pH, and no change in cadmium, copper, and lead concentrations. However, an increase in the other metals tends to support seepage from the ponds.

Table 4.5: Analysis of the geothermal springs.

| Constituent | Pond 5 [mg/L] | Pond 6 [mg/L] |
|---|---|---|
| Cadmium, Total | < 0.0001 | < 0.0001 |
| Cadmium, Dissolved | < 0.0001 | < 0.0001 |
| Calcium, Total | 650 | 720 |
| Calcium, Dissolved | 610 | 690 |
| Copper, Total | < 0.005 | < 0.005 |
| Copper, Dissolved | < 0.005 | < 0.005 |
| Iron, Total | 7.2 | 18 |
| Iron, Dissolved | 7.1 | 5.6 |
| Lead, Total | < 0.005 | < 0.005 |
| Lead, Dissolved | < 0.005 | < 0.005 |
| Magnesium, Total | 92 | 100 |
| Magnesium, Dissolved | 86 | 97 |
| Manganese, Total | 1.1 | 1 |
| Manganese, Dissolved | 1 | 1 |
| Zinc, Total | 0.09 | 0.09 |
| Zinc, Dissolved | 0.07 | 0.07 |
| Sulfate | 970 | 1100 |
| TSS | 290 | 58 |
| TDS | 1300 | 2800 |
| Alkalinity as $CaCO_3$ | 1014 | 1014 |
| pH, s.u. | 6.54 | 6.56 |
| Temperature, C | 34.5 | 45.3 |

Table 4.6: Analysis of channel samples taken up and downstream of observed seepage.

| Constituent | Upstream [mg/L] | Downstream [mg/L] |
|---|---|---|
| Cadmium, Total | < 0.0001 | < 0.0001 |
| Cadmium, Dissolved | < 0.0001 | < 0.0001 |
| Calcium, Total | 53 | 74 |
| Calcium, Dissolved | 49 | 69 |
| Copper, Total | < 0.005 | < 0.005 |
| Copper, Dissolved | < 0.005 | < 0.005 |
| Iron, Total | 0.04 | 0.34 |
| Iron, Dissolved | 0.03 | 0.24 |
| Lead, Total | < 0.005 | < 0.005 |
| Lead, Dissolved | < 0.005 | < 0.005 |
| Magnesium, Total | 6.2 | 8.8 |
| Magnesium, Dissolved | 5.6 | 8 |
| Manganese, Total | 0.011 | 0.58 |
| Manganese, Dissolved | 0.007 | 0.52 |
| Zinc, Total | 0.007 | 0.029 |
| Zinc, Dissolved | 0.005 | 0.024 |
| Sulfate | 59 | 130 |
| TSS | 5 | 5 |
| TDS | 200 | 290 |
| Alkalinity as $CaCO_3$ | 86 | 79.6 |
| pH, s.u. | 8.40 | 7.50 |
| Temperature, C | 11.6 | 15.6 |

## 4.4 Core Sample Analysis

Lime treatment of the St. Louis adit drainage has been occurring since 1984. Moreover, the resulting metal hydroxide sludge has been deposited in the settling ponds during the entire 12 years of operation. Hence, ideal conditions exist for analyzing the long-term effect of this type of treatment on the fate and transport of metals in the sludge. Analysis of the sludge focuses primarily on determining the type, relative quantity, and stability of the metals in the sludge, the compaction of the sludge with depth, and whether diagenetic processes[9] are occurring in the ponds.

In order to determine these long-term effects, it was necessary to sample the entire depth of sludge. Therefore, core samples were taken from ponds 9, 11, and 18, and a grab sample was taken from the pond 5 sediment, where little or no sludge has been deposited. Prior to segmenting the cores into smaller sample sizes, each was visually inspected to determine if stratification within the column was occurring. The cores were then segmented for pore water extraction and metals analysis. Results from the pore water analysis can be found in the Appendix, and only those values that help to support this discussion will be presented here.

## 4.4.1 Visual Description of Cores

Table 4.7 provides a description of each of the cores taken, as well as the total depth of water and sludge within each pond. In addition, photographs of the each of the cores has been provided in Figures 4.7 through 4.11. It was hoped that the sludge would experience reducing conditions at deeper levels in the ponds. If this was the case, then

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[9] Diagenesis refers to the process of physical and chemical change in deposited sediment during its conversion to rock.

black sulfur smelling sludge characteristic of metal sulfides would be predominant, indicating diagenetic processes were occurring. However, it has been observed that ponds 11 through 18 contain an orange, gelatinous, homogeneous mixture of metal hydroxides with occasional swirls and blebs of darker and lighter material. The pond 18 core, illustrated in Figure 4.10, was the most homogenous of the cores taken. It contained some lighter colored swirls but no black color was indicated. However, this core did contain the dark brick-red calcine tailings in the last five centimeters (Figure 4.11). The pond 11 core, illustrated in Figure 4.9, contained more of the darker swirls than the pond 18 core, and no calcine tailings were evident. The pond 9 core, illustrated in Figure 4.8, appears darker and contains some black, sulfur-smelling blebs distributed throughout the column. The pond 5 grab sample, illustrated in Figure 4.7, appears to be mostly pond scum. It was brownish in color but contained some orange specs. All of the cores were soupy at the top of the column, becoming more gelatinous further down. At the bottom of each core, the sludge was more compacted and had a clay like consistency.

Pond 18 contained the deepest sludge. This depth gradually became smaller throughout the pond system, confirming the earlier analysis that most of the precipitate and iron hydroxide floc is settling in ponds 11 through 18.

Table 4.7: Description of the cores taken from ponds 5, 9, 11, and 18.

| Location | Sludge/water depth | Core length | Description |
|---|---|---|---|
| Pond 18 Core | 305 cm / 15 cm (10 ft. / 6 in.) | 243 cm (8 ft.) | A burnt orange color was predominant throughout the column, except for the last six centimeters which was dark brick-red. This is probably remnants of calcine tailings from the acid plant. Contained some swirls and specks of both yellow and red. |
| Pond 11 Core | 180 cm / 150 cm (6 ft. / 5 ft.) | 160 cm ( 5 ft.) | The entire core was orangish/brown in color with a small amount of brick-red and black swirls throughout the column. There was no apparent sulfur odor. |
| Pond 9 Core | 61 cm / 86 cm (2 ft. / 3 ft.) | 40 cm (1.5 ft.) | Consisted primarily of orange sediment, but there were definite coal black blebs and some brownish silt mixed with plants. It was slightly sulfur-smelling. |
| Pond 5 Grab sample | 15 cm / 30 cm (6 in. / 1 ft.) | grab sample | Appears to be pond scum. It was slimy and brownish in color with some orange specs. Sample contained a small amount of plants. |

Figure 4.7: Photograph of the grab sample from pond 5 sediments.

Figure 4.8: Photograph of the core taken from pond 9.

Figure 4.9: Photograph of the core taken from pond 11.

Figure 4.10: Photograph of the core taken from pond 18.

Figure 4.11: Photograph of the calcine tailings in the bottom of the core from pond 18

### 4.4.2 Metals Analysis of the Cores

Since the cores appeared homogeneous, only representative samples from the top, middle, and bottom of each core and associated pore waters were analyzed for metal concentrations, and other relevant constituents. Figures 4.12, 4.13, 4.14, and 4.15 illustrate the metals concentrations in the sediment and pore waters for ponds 5, 9, 11, and 18, respectively. These concentrations are also listed in the Appendix. From these bar charts it appears that most of the metal concentrations are equal, within the 20% error dictated by the analytical laboratory. The slight increase in Cd, Cu, Pb, and Zn in the upper half of the pond 18 core could indicate the change in liming techniques that occurred in 1986, providing more efficient metal removal with a slaking reactor as apposed to simple lime addition. However, it will be assumed that the cores are approximately homogeneous throughout the column, and the remaining analysis will be based on this assumption.

Table 4.8 contains a distribution of each metal found in each of the pond sediment samples. Since homogeneity has been assumed for the cores taken from ponds 9, 11, and 18, an average concentration within the core was used. These percentages are relative to the total metal concentration in each core.

Table 4.8: Comparison of metal concentrations relative to the total concentration in each pond.

| Constituent | Pond 5 | Pond 9 | Pond 11 | Pond 18 |
|---|---|---|---|---|
| Cadmium | 0.09% | 0.04% | 0.06% | 0.04% |
| Calcium | 8.67% | 29.40% | 10.23% | 48.49% |
| Copper | 0.32% | 0.31% | 0.67% | 0.51% |
| Iron | 48.18% | 54.19% | 68.55% | 35.24% |
| Lead | 0.14% | 0.14% | 0.32% | 0.11% |
| Magnesium | 2.12% | 1.04% | 1.42% | 5.14% |
| Manganese | 31.80% | 7.03% | 6.06% | 2.60% |
| Zinc | 8.67% | 7.84% | 12.70% | 7.87% |
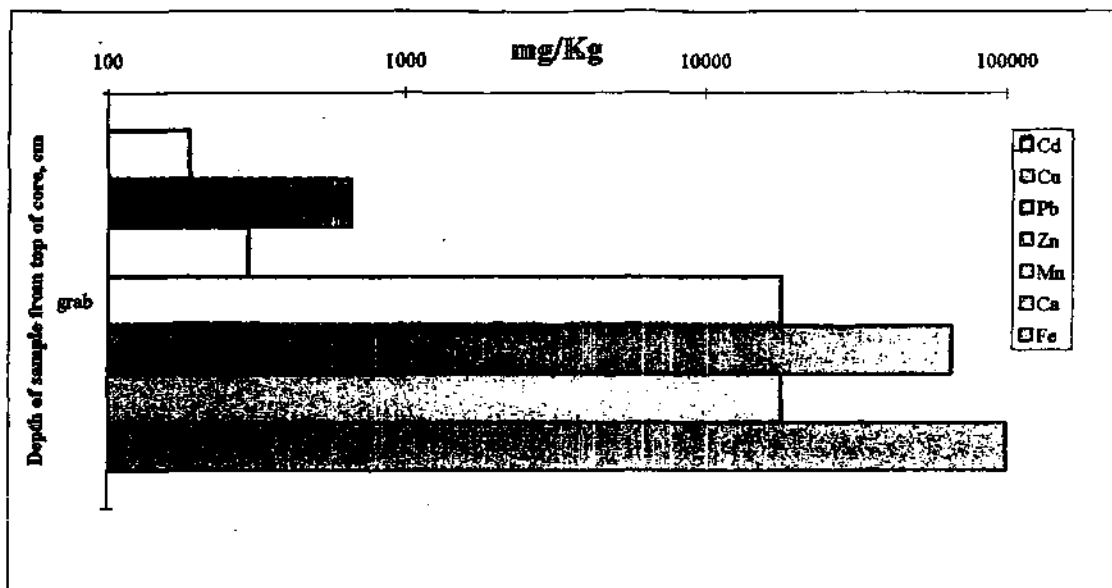
Figure 4.12a. Metal concentrations in pond 5 sediment sample.
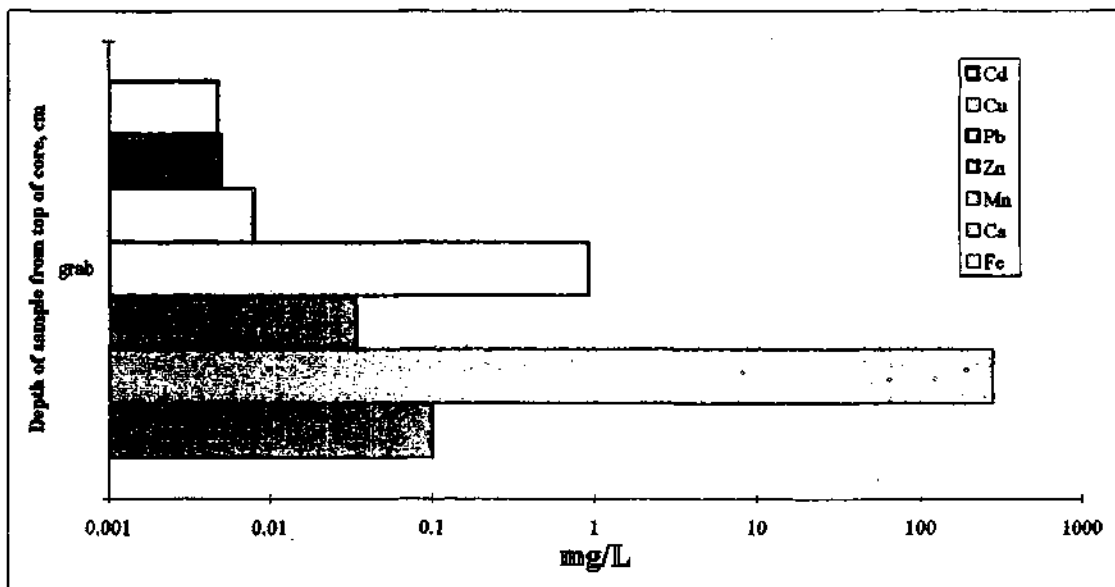


Figure 4.12b. Metal concentrations in pond 5 pore water sample.
Concentrations are also listed in the Appendix.
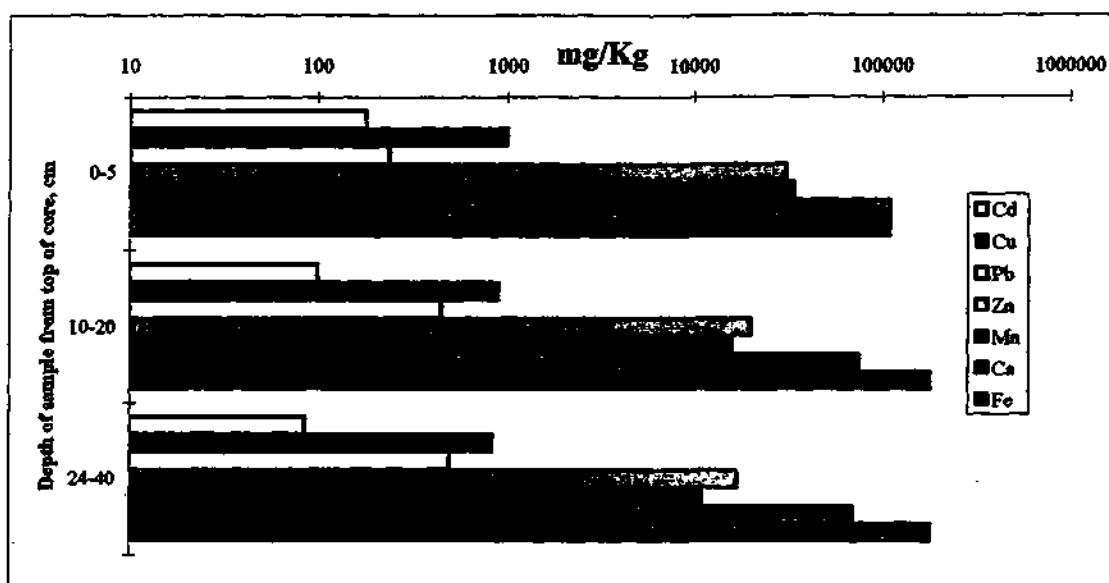
Figure 4.13a. Metal concentrations in pond 9 sediment samples.
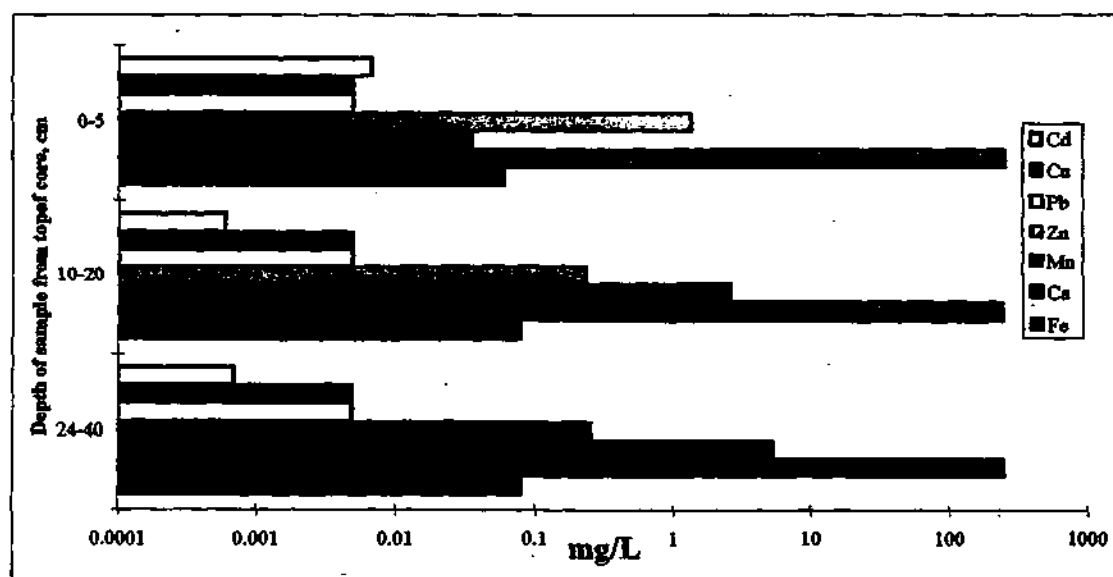


Figure 4.13b. Metal concentrations in pond 9 pore water samples.
Concentrations are also listed in the Appendix.
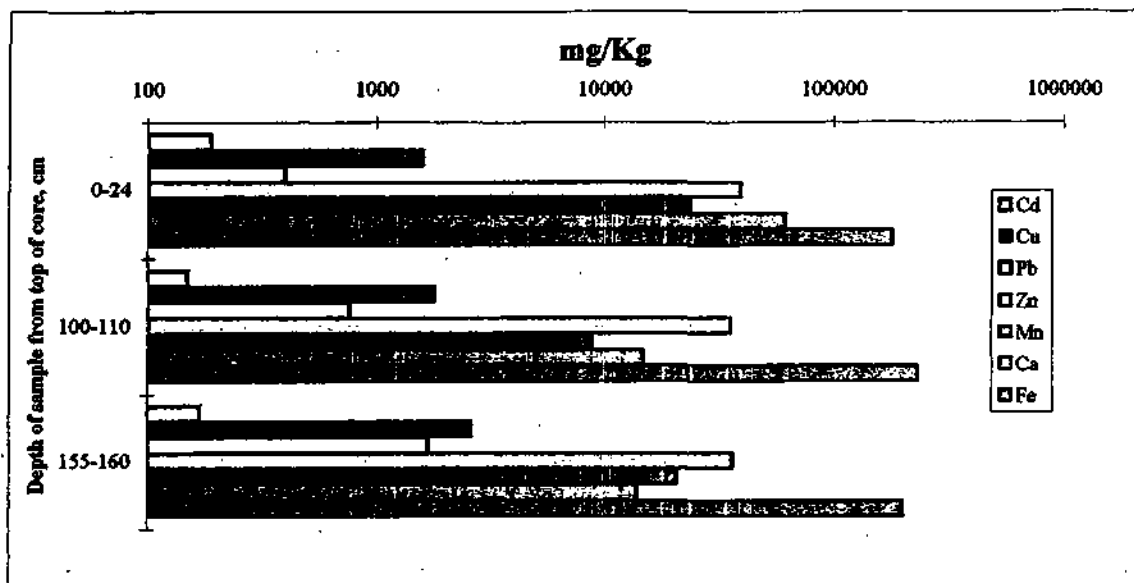
Figure 4.14a. Metal concentrations in pond 11 sediment samples.
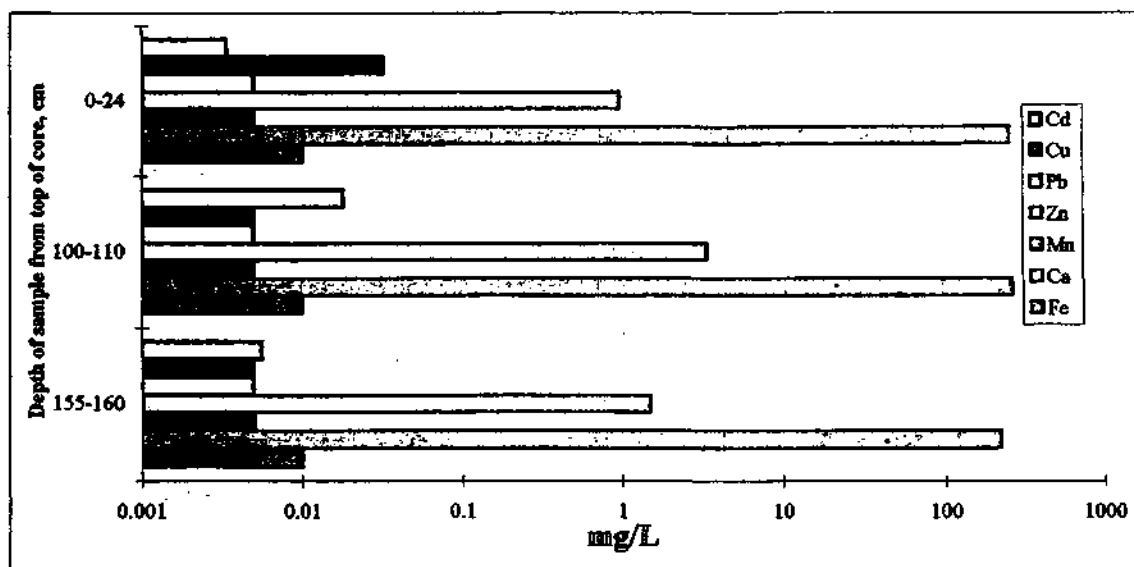


Figure 4.14b. Metal concentrations in pond 11 pore water samples.
Concentrations are also listed in the Appendix.
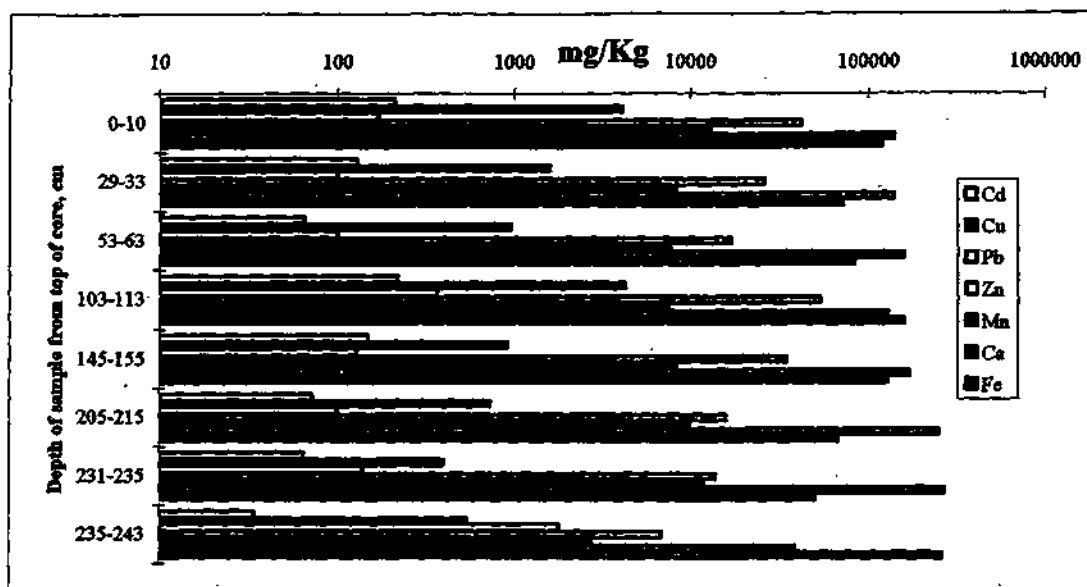
Figure 4.15a. Metal concentrations in pond 18 sediment samples.
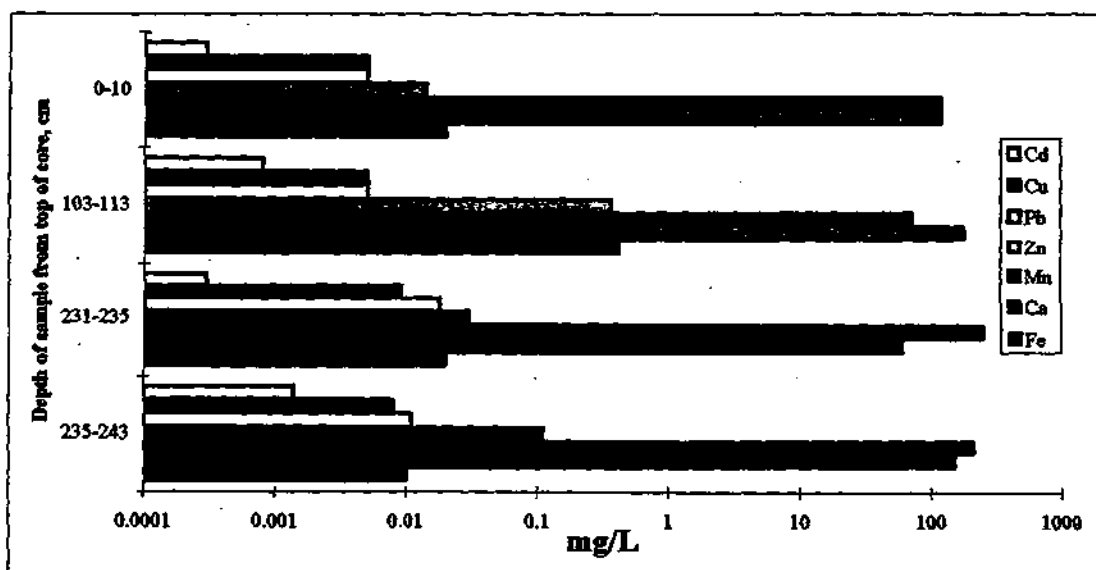


Figure 4.15b. Metal concentrations in pond 18 pore water samples.
Concentrations are also listed in the Appendix.

Despite the fact that metal concentrations appear to be similar within each individual core, a comparison of concentrations from pond to pond indicate some variability. The sediments in ponds 9, 11, and 18 contain mostly calcium and iron floc. However, manganese and zinc also have a strong presence. Although pond 5 also contains elevated concentrations of iron, high concentrations of manganese rather than calcium accompanies the iron. In fact, it appears that manganese concentrations gradually increase in the sediment in the downstream direction. The concentrations of cadmium, copper, and lead are virtually non-existent relative to the other metals in all the ponds.

Pore waters for all the core samples are elevated in calcium. However, in samples from ponds 5 and 11 zinc is the next predominant metal. In ponds 9 and 18 manganese is the second most predominant metal. All the pore waters tend to be low in cadmium, copper, and lead, but higher in zinc.

Probably the most important quality of any sludge is its stability. Those sludges that pass the Characteristic Leaching Procedure (TCLP) test are considered non-hazardous, and thus are much easier to dispose of. In late May of 1995, PTI Environmental Service of Boulder, Colorado sampled and tested surficial sediments in ponds 5, 11, and 18. (Filipek 1995). The TCLP extractable metal concentrations from this test along with concentration limits are given in Table 4.9 (ibid.).

Table 4.9:   Concentrations of sediment TCLP extracts..
Source:  Filipek 1995.

| METAL | POND 5 mg/L | POND 11 mg/L | POND 18 mg/L | TCLP LIMIT, mg/L |
|-------|-------------|--------------|--------------|-------------------|
| Barium | 0.5 | < 0.4 | < 0.4 | 100.0 |
| Cadmium | < 0.01 | 0.02 | 0.03 | 1.0 |
| Chromium | < 0.01 | < 0.01 | 0.01 | 5.0 |
| Lead | 0.5 | < 0.05 | < 0.05 | 5.0 |
| Mercury | <0.0002 | < 0.0002 | < 0.0002 | 0.2 |
| Silver | < 0.01 | < 0.01 | < 0.01 | 5.0 |

These results clearly indicate that the surficial sediments can be considered stable, but it does not confirm that the entire depth of sludge is also stable. Perhaps the dredged sediments located in the new pond north of the site would provide a more representative sample for TCLP test. This test was not performed in this study.

### 4.4.3 Solids Content Determinations and Density Estimation of the Cores

The solids content and density have been determined for cores taken from ponds 11 and 18. Results from the laboratory analysis and estimation of these parameters for each core were combined to determine the average density of the sludge, and a mathematical relationship between pond depth and moisture content. Table 4.10 contains the results of the bulk density estimations, and Figure 4.6 illustrates the functional relationship between the moisture content of the sludge and depth.

Bulk densities of the individual sludge samples were estimated to be the weighted average of the water and solids in the sample:

$$\rho_{bulk} = x_{solid}\rho_{solid} + x_{water}\rho_{water}$$

Here, the mass fraction of the solid is the percent solids determined analytically, and the density is assumed to be the average of the density of calcium carbonate (SG = 1.7) and iron hydroxide (SG = 3.2). By calculating the bulk densities in this fashion, the estimated values increase with increasing depth, as was observed of the cores in the field.

The moisture content was determined experimentally by heating the sample enough to drive off any free water present, and then calculating the difference between the wet weight and dry weight of the samples. The resulting exponential fit, Figure 4.16, is consistent with observations of marine and lake sediments (Berner, 1980).

Table 4.10: Bulk density estimates for the combined cores from ponds 11 and 18.

| Average core depth, cm | Bulk Density, $Kg/m^3$ | Average core depth, cm | Bulk Density, $Kg/m^3$ |
|---|---|---|---|
| 5 | 1085 | 112 | 1092 |
| 12 | 1094 | 118 | 1083 |
| 12 | 1078 | 118 | 1144 |
| 16 | 1062 | 128 | 1079 |
| 20 | 1064 | 128 | 1177 |
| 24 | 1106 | 134 | 1279 |
| 26 | 1091 | 136 | 1239 |
| 28 | 1137 | 140 | 1277 |
| 30 | 1089 | 141 | 1266 |
| 31 | 1145 | 145 | 1425 |
| 38 | 1133 | 149 | 1282 |
| 41 | 1267 | 150 | 1247 |
| 48 | 1110 | 153 | 1128 |
| 51 | 1238 | 158 | 1220 |
| 58 | 1148 | 160 | 1164 |
| 61 | 1183 | 170 | 1169 |
| 68 | 1423 | 180 | 1278 |
| 71 | 1114 | 190 | 1259 |
| 78 | 1104 | 200 | 1265 |
| 81 | 1078 | 210 | 1178 |
| 88 | 1191 | 217 | 1227 |
| 88 | 1123 | 221 | 1298 |
| 96 | 1129 | 225 | 1241 |
| 98 | 1303 | 229 | 1351 |
| 106 | 1147 | 233 | 1392 |
| 108 | 1157 | | |

Average bulk density ==> 1187
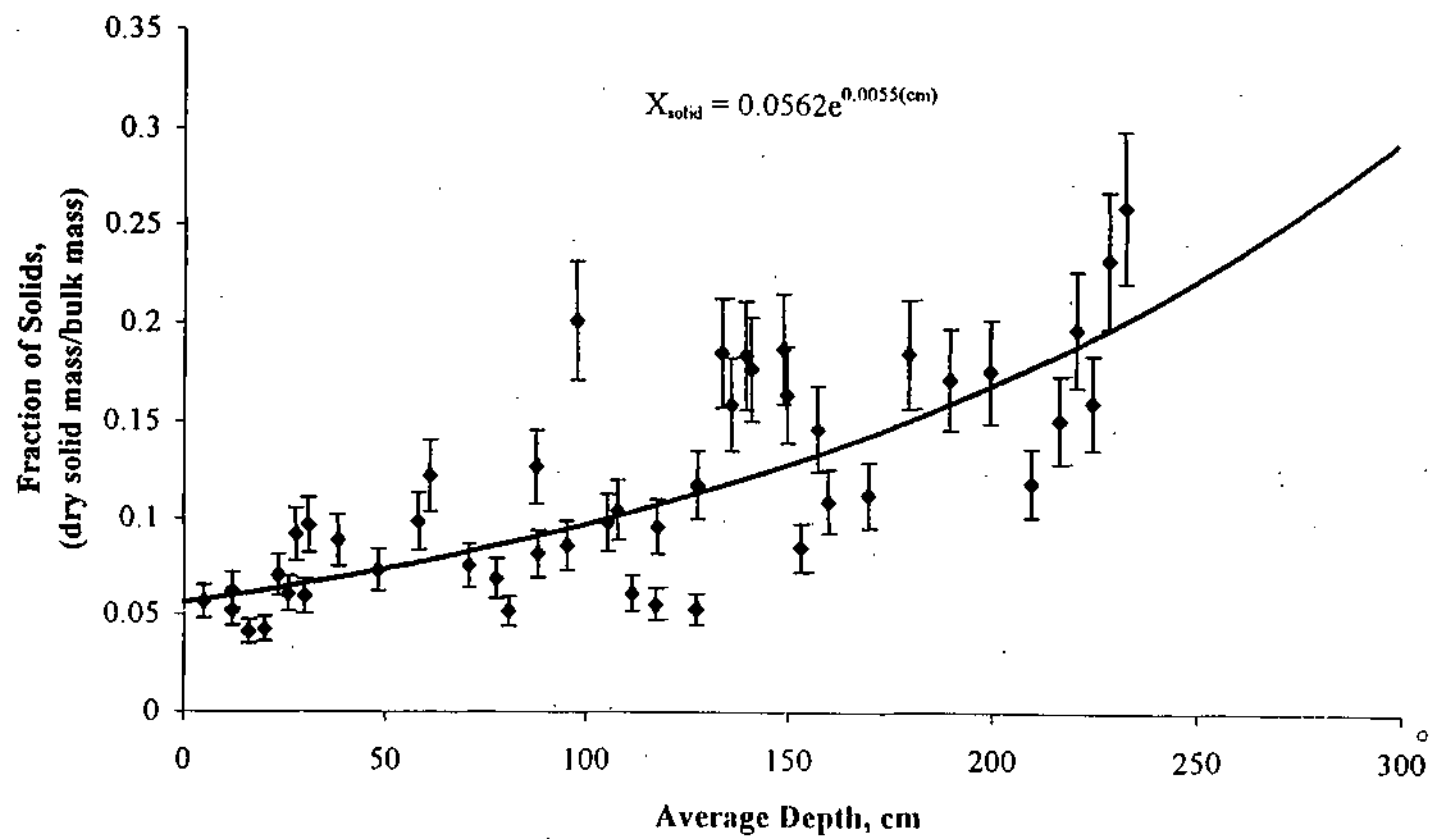
Figure 4.16: Moisture content of the sludges in ponds 11 and 18.

The plotted curve follows the relation $X_{solid} = 0.0562e^{0.0055(cm)}$.

## 4.5 Engineering Design Analysis

An engineering analysis of the physical properties of the pond system was performed. This involved the application of scientific and mathematical principles, resulting in practical design parameters for use in analyzing and proposing improvements in the efficiency of the system. The results provided here include an estimate of the empty and sludge volumes of the ponds, an evaluation of historical flow rate data for the development of stabilization basin parameters, and a correlation between the residence time of water in the system and the effective volume.

### 4.5.1 Estimate of Empty and Sludge Volumes of the Ponds

The pond volumes were estimated by applying both geometric and trigonometric functions to dimensions measured at the site and from the site topography map (Figure 1.2) and are listed in Table 4.11. Site measurements included both total and sludge depths in ponds 5, 9, 11 and 18 (Table 4.7). The depths of the remaining ponds were extrapolated from these values. The site topography map provided the surface area of each pond (Table 4.3).

The geometry of each pond was assumed to be similar to the frustum of a right circular cone (Figure 4.17), having a volume of:

$$V = 1/3 \; \pi \; h \; (r_1^2 + r_1 r_2 + r_2^2)$$

Here, h is the measured depth of the ponds, $r_1$ is the radius of the assumed circular surface estimated by the topography map, and $r_2$ is the radius of the bottom of the ponds. Neither the radius of the bottom of the ponds or the lengths (S) of the berms were
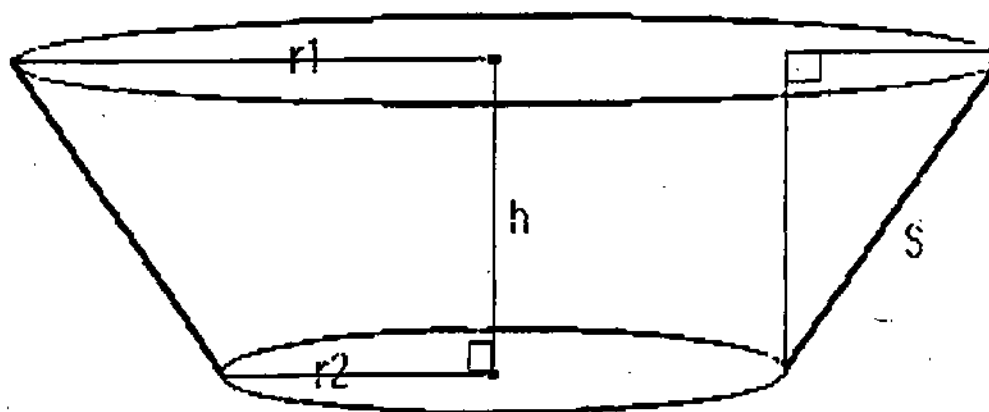
Figure 4.17: Assumed geometry of the ponds.

measured. However, by assuming the slope of the berm is 1 and recognizing that the length of the hypotenuse of a right triangle is equal to the square root of the sum of the sides squared, the berm length and bottom radius can be calculated as follows:

$$S = (2)^{1/2} h$$
$$r_2 = r_1 - (S^2 - h^2)^{1/2}$$

Results from this calculation indicate that the total empty pond volume is 2,810,000 cubic feet, and the total volume of sludge in the ponds is 1,840,000 cubic feet (Table 4.11).

Table 4.11: Estimated volume of the ponds and sludge.

| Pond | Empty Volume, ft$^3$ | Sludge volume, ft$^3$ |
|---|---|---|
| 18 | 780,000 | 660,000 |
| 15 | 660,000 | 560,000 |
| 14 | 240,000 | 130,000 |
| 12 | 320,000 | 170,000 |
| 11 | 240,000 | 130,000 |
| 9 | 70,000 | 30,000 |
| 8 | 150,000 | 50,000 |
| 7 | 200,000 | 70,000 |
| 6 | 90,000 | 30,000 |
| 5 | 60,000 | 10,000 |
| Total | 2,810,000 | 1,840,000 |

## 4.5.2 Stabilization Pond Parameters

A stabilization pond was considered for this site due to the large seasonal variability of flow rates. Data gathered from monitoring reports at the treatment plant in Rico, Colorado, indicate that flow rates in May, June, July, and August can be as much as two times higher than any other time of year. Figure 4.18 illustrates the monthly average flow rates at the CPDES outfall, for nine of the last twelve years. Tabulated values have been provided in the Appendix. For the purpose of determining stabilization basin parameters, the monthly flow rates were averaged over 9 years. These averages are displayed in Table 4.12.

The design parameters determined for a stabilization pond at this site, included the necessary pond volume, and the required uniform effluent from this pond. These parameters were calculated numerically by the application of a material balance around a proposed pond.
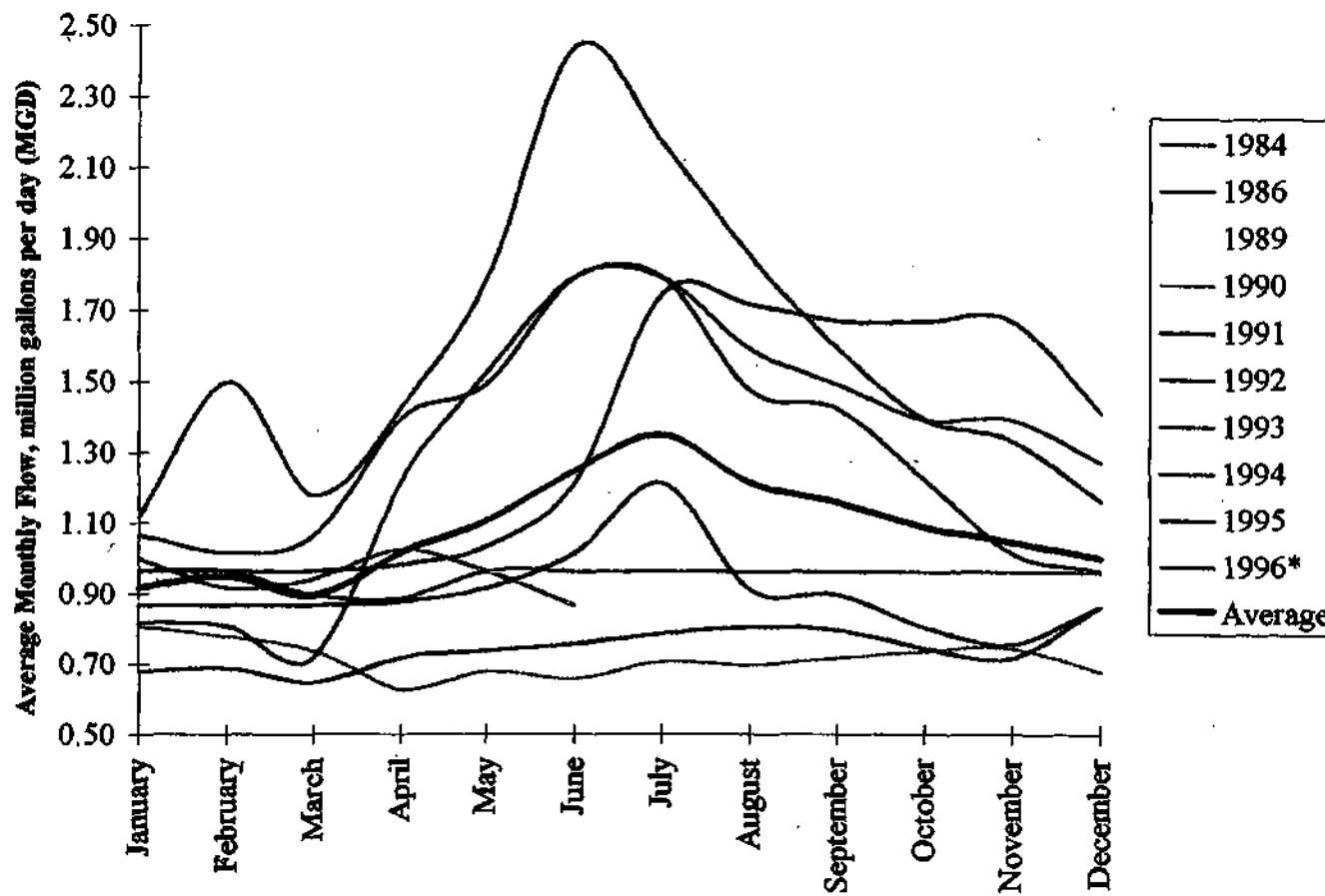
Figure 4.18: Flow rates measured at the CPDES Outfall, 1984-1996.
*1996 is only through June.

Table 4.12: Nine year average of monthly flow rates measured at CPDES Outfall 002, at the St. Louis settling ponds. Adit flow rates are typically 40% larger.

|  | MGD[a] |
| --- | --- |
| January | 0.92 |
| February | 0.95 |
| March | 0.90 |
| April | 1.02 |
| May | 1.11 |
| June | 1.25 |
| July | 1.35 |
| August | 1.22 |
| September | 1.16 |
| October | 1.09 |
| November | 1.05 |
| December | 1.01 |

[a] Million gallons per day

Recognizing the control volume as the proposed stabilization pond, and the sole input and output values as the adit drainage ($Q_{in}$), and the yet undetermined uniform effluent ($Q_{out}$), respectively, the material balance becomes:

$$dS/dt = Q_{in} - Q_{out}$$

In this derivation, dS/dt is the accumulation of water over time in the storage basin, and it has been assumed that the density of water is constant. Multiplying both sides by dt, and substituting finite time increments ($\Delta t$) equal to the number of days in a given month, the resulting equation is:

$$\Delta S = (Q_{in} - Q_{out})\Delta t$$

The units associated with each term are now in volumes instead of volumetric flow rates. Hence, by subtracting the monthly input and output volumes and summing over the months of the year where the influent is greater than the effluent, the required volume can be determined. This has been illustrated graphically in Figure 4.19, and is accompanied with the tabulated calculation. The area between the curves where the adit drainage is greater than the uniform effluent, is the required volume of a pond to stabilize the flow. In essence, this summation procedure is the integral between the two volume curves.

Because the uniform effluent was also unknown, the equation had to be solved repeatedly, by selecting a uniform flow, and calculating the required storage volume, until a minimum value was reached. The constraint of the iteration was that $\Sigma\Delta S$, could increase or decrease throughout the calculation, but it could never be less than zero. This would be a physical impossibility, since at zero the pond would be empty.

Results indicate that the minimum volume requirement for stabilizing the adit drainage would be approximately 20 million gallons (2.8 million cubic feet), with a uniform effluent flow of 1.09 million gallons per day (757 gpm). To put this into perspective, the total empty volume of the entire pond system is approximately 21 million gallons. Hence, a stabilization pond would require approximately 95% of the total volume of ponds currently existing at the site. Moreover, this estimate was based on the CPDES Outfall flow rates which appears to be approximately 40% lower than the adit drainage flow rates. Hence, this estimate is lower than what would actually be needed, but does demonstrate that the area needed to stabilize seasonal flows is considerable.
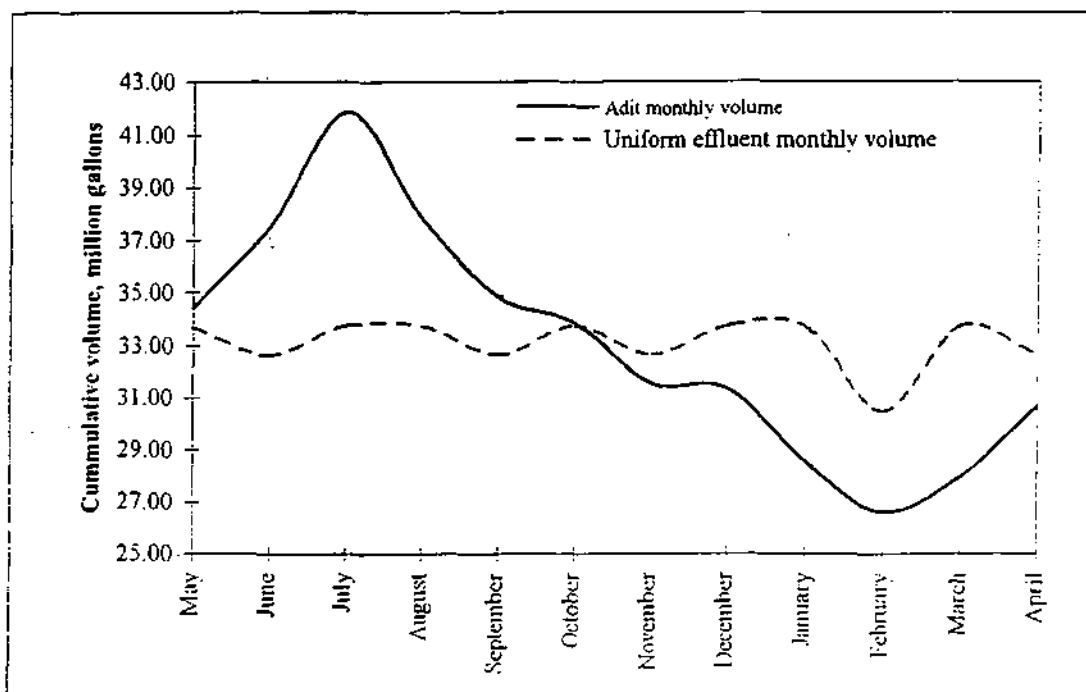
| Month | Adit monthly flow rate, MGD[a] | Uniform effluent flow rate, MGD | Days in the month | Adit monthly volume, MG[b] | Uniform effluent monthly volume, MG | Monthly storage requirement $\Delta S$, MG | Annual storage requirement $\Sigma \Delta S$, MG |
|---|---|---|---|---|---|---|---|
| May | 1.11 | 1.087 | 31 | 34.41 | 33.68 | 0.73 | 0.73 |
| June | 1.25 | 1.087 | 30 | 37.50 | 32.60 | 4.91 | 5.63 |
| July | 1.35 | 1.087 | 31 | 41.85 | 33.68 | 8.17 | 13.80 |
| August | 1.22 | 1.087 | 31 | 37.82 | 33.68 | 4.14 | 17.94 |
| September | 1.16 | 1.087 | 30 | 34.80 | 32.60 | 2.21 | 20.15 |
| October | 1.09 | 1.087 | 31 | 33.79 | 33.68 | 0.11 | 20.25* |
| November | 1.05 | 1.087 | 30 | 31.50 | 32.60 | -1.10 | 19.16 |
| December | 1.01 | 1.087 | 31 | 31.31 | 33.68 | -2.37 | 16.78 |
| January | 0.92 | 1.087 | 31 | 28.52 | 33.68 | -5.16 | 11.62 |
| February | 0.95 | 1.087 | 28 | 26.60 | 30.42 | -3.82 | 7.80 |
| March | 0.90 | 1.087 | 31 | 27.90 | 33.68 | -5.78 | 2.02 |
| April | 1.02 | 1.087 | 30 | 30.60 | 32.60 | -2.00 | 0.02 |

*Required volume of a stabilization pond

[a]Million gallons per day

[b]Million gallons

Figure 4.19: Graphical representation of stabilization volume requirements and the accompanying numerical integration.

### 4.5.3 Analysis of the Water Retention Time and Effective Settling Volume in the Ponds

Sedimentation is utilized at the St. Louis site for the removal of coagulated and flocculated particles from the water prior to discharge into the Dolores River. The theory of sedimentation is the theory of the effect of gravity on the particles suspended in the water. Given enough time in the settling ponds, particles having a density greater than water will settle under the influence of gravity. Therefore, the effluent quality is strongly dependent on the retention time of the water in the system. However as the ponds fill with sludge, short-circuiting occurs and the retention time is reduced, resulting in higher metals concentrations down stream. Eventually, the constituents of concern will find their way into the river, as the volume available for settling (effective volume, Ve) declines.

A correlation between the retention time and effective volume of the ponds at the St. Louis site has been established to demonstrate the limited lifetime of the ponds under the current treatment conditions. This correlation was developed by performing a material balance on ponds 11 through 18, with the adit drainage and the CPDES outfall as the input and output, respectively. Only the upper ponds in the system were selected because of observations that a majority of the metals and solids are settling in these ponds, and the reduction in residence time is most likely occurring there.

By assuming that the system is at steady state with respect to water, pseudo-steady state conditions are established where only the accumulation of solids is occurring. Assuming further that the density of the sludge in the ponds is constant, and substituting an incremental time interval of 1 year ($\Delta t$) for dt, the resulting material balance on the system is:

$$\Delta V_e = (m_{sin} - m_{sout})/\rho_s \; \Delta t$$

Here $(m_{sin}-m_{sout})/\rho_s$ is the accumulation of sludge in the system over one year, in ft$^3$/year. This value is easily calculated from the previously determined volumes in Table 4.11, and is equal to the total sludge volume in Ponds 11-18 divided by twelve years. It has been assumed that the sludge has accumulated due solely to the twelve year operation of the lime treatment plant, and primarily in ponds 11 through 18. Alternatively, the liming rates and metal loading rates could be used as input terms. However, metal loading rates over the last 12 years are not known. By summing this value over several years the effect is a filling of the ponds, and a reduction of the effective volume by the equation:

$$V_e = V_T - \Sigma \Delta V_s$$

Here $V_T$ is the total empty volume of the ponds 11 through 18, in ft$^3$ (Table 4.11). The retention time ($\tau$) can then be calculated for each successive year of operation by dividing the effective volume by the flow rate of water into the system ($Q_w$):

$$\tau = V_e / Q_w$$

Here $Q_w$ is assumed to be constant and equal to the average of the nine year average of monthly flow rates measured at CPDES Outfall 002, and listed in Table 4.12.

Figure 4.20 illustrates the reduction of the residence time through twelve years of operation and is accompanied by the tabulated calculations of the effective volume. Although this is a crude estimate of these parameters, it demonstrates the importance of maintaining enough volume in the ponds to facilitate gravitational settling.

Based on these calculations, it appears that the residence time has decreased by 74%. In addition, if liming continues as is, these ponds could be full in as little as 4 years.
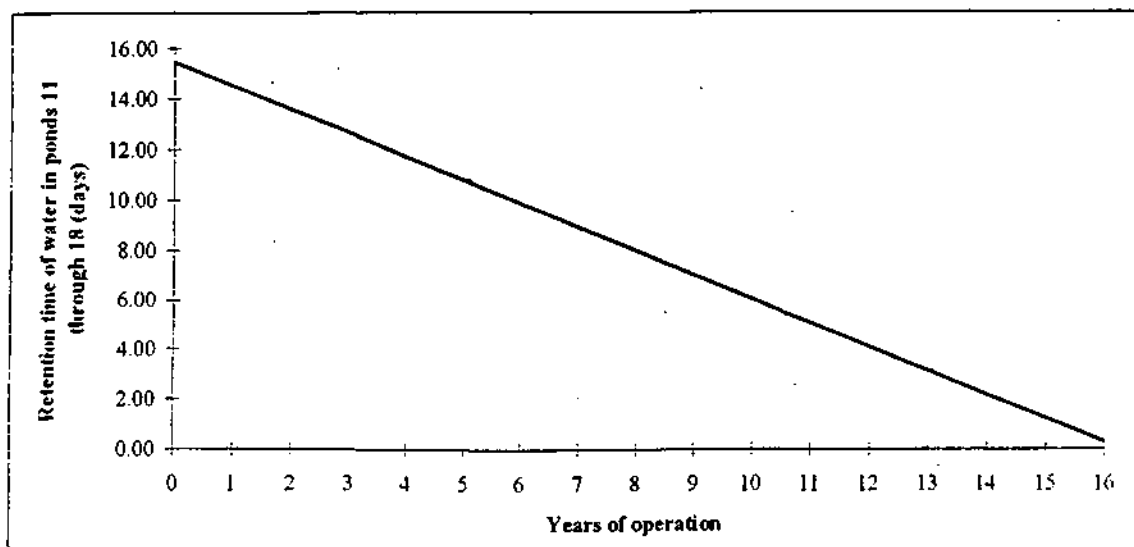
Empty volume of the ponds 11 through 18 (Vt) = 2,240,000 ft³
Average annual adit flow rate (Qw) = 145,000 ft³/day

| Year | Annual solids production Vs, ft³ | Cummulation of solids in ponds Vs, ft³ | Effective volume, Ve (Vt - Vs), ft³ | Residence time, τ Ve/Qw, days |
|---|---|---|---|---|
| 0 | 0 | 0 | 2,240,000 | 15.45 |
| 1 | 137,500 | 137,500 | 2,102,500 | 14.50 |
| 2 | 137,500 | 275,000 | 1,965,000 | 13.55 |
| 3 | 137,500 | 412,500 | 1,827,500 | 12.60 |
| 4 | 137,500 | 550,000 | 1,690,000 | 11.66 |
| 5 | 137,500 | 687,500 | 1,552,500 | 10.71 |
| 6 | 137,500 | 825,000 | 1,415,000 | 9.76 |
| 7 | 137,500 | 962,500 | 1,277,500 | 8.81 |
| 8 | 137,500 | 1,100,000 | 1,140,000 | 7.86 |
| 9 | 137,500 | 1,237,500 | 1,002,500 | 6.91 |
| 10 | 137,500 | 1,375,000 | 865,000 | 5.97 |
| 11 | 137,500 | 1,512,500 | 727,500 | 5.02 |
| 12 | 137,500 | 1,650,000 | 590,000 | 4.07 |
| 13 | 137,500 | 1,787,500 | 452,500 | 3.12 |
| 14 | 137,500 | 1,925,000 | 315,000 | 2.17 |
| 15 | 137,500 | 2,062,500 | 177,500 | 1.22 |
| 16 | 137,500 | 2,200,000 | 40,000 | 0.28 |

Figure 4.20: Residence time of the drainage in ponds 11 through 18 over sixteen years of lime treatment and settling, with accompanying effective volume calculation.

## 4.6  Modeling Results

Geochemical and process modeling was performed on the adit drainage and lime treatment plant, respectively. The purpose of the geochemical modeling was to gain a better understanding of the chemical state of the constituents in the mine water. In addition, results from this model provided information regarding the chemical reactions occurring, and the type of solids that could potentially precipitate.

Results from the geochemical modeling were then used to investigate the applicability of a chemical engineering process model to the lime treatment of the drainage. It was hoped that the process modeling would provide a predictive tool for use in determining the applicability of alternative processes, in addition to optimizing the current treatment plant.

This section provides a discussion of the models used, the input parameters required for each model, and the subsequent results.

### 4.6.1  Geochemical Modeling with MINTEQA2

Geochemical modeling was performed using MINTEQA2 version 3.11, distributed by the International Ground Water Modeling Center (IGWMC), at the Colorado School of Mines. Table 4.13 lists the input parameters conveyed to the model. These values are those measured from samples taken at the St. Louis adit prior to liming. In addition to those constituents listed, the Davies equation was selected as the method for computing activity coefficients.

Results from the MINTEQA2 modeling pertinent to this study included a distribution of the components in the dissolved state (Table 4.14), as well as the saturation

index of potential solids (Table 4.15). The saturation index is the logarithmic ratio of the ion activity products and the equilibrium formation constant for a specified solid in a given precipitation reaction, and indicates the saturation state of the solid. Positive values suggest that the water is supersaturated for this component and precipitation will occur. Negative values suggest the water is undersaturated and the component will remain in the dissolved state unless equilibrium shifts to a state more favorable for precipitation.

In addition to providing an approximation of species present for use in the process model, these results provide some insight into the nature of the adit drainage. For instance, the orange floc present in the drainage is probably iron and manganese hydroxides and manganese carbonate. These are the solids that exhibit a positive saturation index. Furthermore, most of the metals are present in the dissolved state as either free ions, or hydroxide, carbonate, and sulfate complexes. Chloride and sodium don't appear to play a significant role in the overall chemistry of the drainage. This is consistent with the water quality data which indicates that chloride and sodium are relatively constant throughout the ponds.

Table 4.13: Input parameters for MINTEQA2 geochemical modeling.

| Parameter | Value |
|---|---|
| Temperature, °C | 18.6 |
| pH, s.u. | 6.29 |
| Alkalinity, mg/L as $CaCO_3$ | 77.2 |
| $Cd^{2+}$, mg/L | 0.025 |
| $Ca^{2+}$, mg/L | 210 |
| $Cu^{2+}$, mg/L | 0.31 |
| $Fe^{3+}$, mg/L | 16 |
| $Pb^{2+}$, mg/L | 0.018 |
| $Mg^{2+}$, mg/L | 20 |
| $Mn^{3+}$, mg/L | 3.2 |
| $Zn^{2+}$, mg/L | 4 4 |
| $K^-$, mg/L | 1.5 |
| $Na^+$, mg/L | 7.1 |
| $SO_4^{2-}$, mg/L | 420 |
| $CL^-$, mg/L | 3 |

Table 4.14: Percentage distribution of constituents in the St. Louis adit drainage as predicted by MINTEQA2 equilibrium modeling.

| Constituent | Distribution |
|---|---|
| $Cd^{2+}$ | 72% $Cd^{2+}$ |
| | 23% $CdSO_4$ aq. |
| | 4% $CdHCO_3^-$ |
| $Ca^{2+}$ | 82% $Ca^{2+}$ |
| | 18% $CaSO_4$ aq. |
| $Cu^{2+}$ | 60% $Cu^{2+}$ |
| | 11% $CuCO_3$ aq. |
| | 3% $Cu(OH)_2$ aq. |
| | 13% $CuSO_4$ aq. |
| | 12% $CuHCO_3^+$ |
| $Fe^{3+}$ | 98% $FeOH_2$ |
| | 2% $Fe(OH)_3$ aq. |
| $Pb^{2+}$ | 38% $Pb^{2+}$ |
| | 25% $PbSO_4$ aq. |
| | 23% $PbCO_3$ aq. |
| | 12% $PbHCO_3^-$ |
| $Mg^{2+}$ | 83% $Mg^{2+}$ |
| | 16% $MgSO_4$ aq. |
| $Mn^{3+}$ | 100% $Mn^{3+}$ |
| $Zn^{2+}$ | 76% $Zn^{2+}$ |
| | 19% $ZnSO_4$ aq. |
| | 4% $ZnHCO_3^-$ |
| $K^+$ | 99% $K^+$ |
| | 1% $KSO_4^-$ |
| $Na^+$ | 100% $Na^+$ |
| $SO_4^{2-}$ | 75% $SO_4^{2-}$ |
| | 3% $MgSO_4$ aq. |
| | 22% $CaSO_4$ aq. |
| $CO_3^{2-}$ | 51% $HCO_3^-$ |
| | 48% $H_2CO_3$ aq. |
| | 1% $CaHCO_3^+$ |
| $H^+$ | 35% $HCO_3^-$ |
| | 65% $H_2CO_3$ aq. |
| $Cl^-$ | 100% $Cl^-$ |

Table 4.15: Saturation indices of potential solids in the St. Louis adit drainage as predicted by MINTEQA2 equilibrium modeling.

| Potential Solid | Saturation Index |
|---|---|
| $Cd(OH)_2$ | -8.150 |
| $CdCO_3$ | -0.583 |
| $CdSO_4$ | -9.928 |
| $Cu(OH)_2$ | -3.713 |
| $CuSO_4\text{-}5H_2O$ | -7.456 |
| $Pb(OH)_2$ | -4.055 |
| $PbCO_3$ | -2.286 |
| $PbSO_4$ | -3.146 |
| $Zn(OH)_2$ | -4.000 |
| $ZnCO_3$ | -1.505 |
| $ZnSO_4\text{-}7H_2O$ | -5.229 |
| $Fe(OH)_3$ | 2.185 |
| $FeO(OH)$ | 6.344 |
| $MnO(OH)$ | 14.319 |
| $Mn_2(CO_3)_3$ | 28.528 |
| $Mn_2(SO_4)_3$ | -12.627 |
| $Ca(OH)_2$ | -13.185 |
| $CaCO_3$ | -1.551 |
| $CaSO_4$ | -0.731 |
| $CaSO_4\text{-}2H_2O$ | -0.455 |
| $Mg(OH)_2$ | -8.041 |
| $MgCO_3$ | -2.718 |
| $MgSO_4\text{-}7H_2O$ | -3.939 |

### 4.6.2 Process Modeling with ASPEN Plus

Process modeling was performed using ASPEN Plus Release 9, developed and distributed by Aspen Technology, Inc. of Cambridge, Ma. Figure 4.21 is an illustration of the process flow diagram used to model the lime treatment of the adit drainage. It contains a splitting unit for diverting water from the adit to the treatment plant, a mixing unit for reacting the lime with the diverted water, and another mixing unit for the re-addition of the lime slurry to the adit drainage. Thirty percent (800 gpm) of the original adit flow rate (2200 gpm) was diverted to the lime reactor. The flow rate values selected were based on flow rate measurements listed in Table 4.1. Lime was added to the lime reactor at a constant rate of 600 lbs/day CaO. To simplify the reaction mechanisms required for this model, hydrated lime, $Ca(OH)_2$, was substituted for CaO in stoichiometric amounts. Values for the constituents in the adit stream were derived from the adit sample concentrations. The combined adit and slurry streams were allowed to reach equilibrium similar to what would occur in the pond system. Hence, the final product stream concentrations should compare to the CPDES outfall concentrations measured in the field. In addition, if no lime is added to the system, the final product stream should contain concentrations similar to the adit concentrations.

Comparisons between the modeling results and the values measured in the field can be found in Figure 4.22. These results indicate that the model is in fairly good agreement with measured values for alkalinity, pH, magnesium and calcium. However, large discrepancies occur with zinc, manganese, lead, copper, cadmium, and iron. This is due primarily to the fact that the model was limited in the number of constituent and chemical reactions it could accommodate at one time. When attempts were made to convey all the constituents and potential reactions involving these constituents as demonstrated by the geochemical modeling, the system failed to function. Hence, it became necessary to remove some reactions and components. An input summary has been
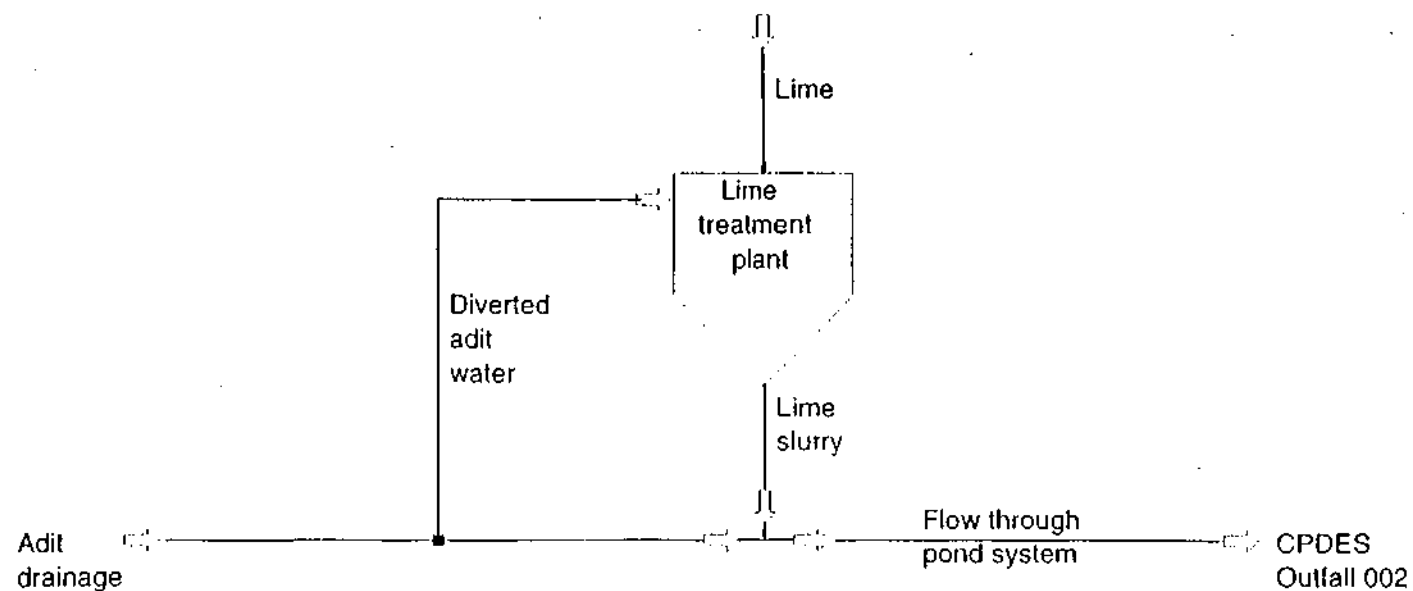
Figure 4.21: Process flow diagram for modeling the lime treatment plant using ASPEN Plus.
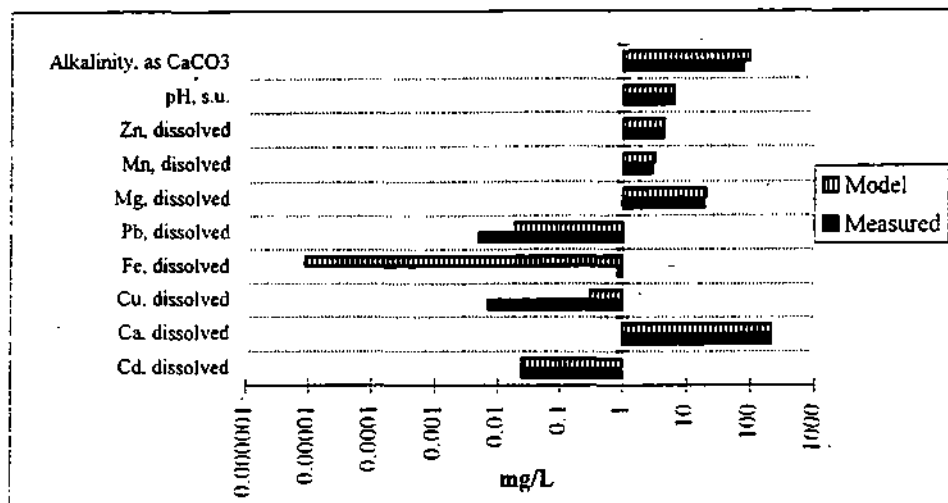
Figure 4.22a. Comparison of measured and modeled concentrations in the adit drainage.
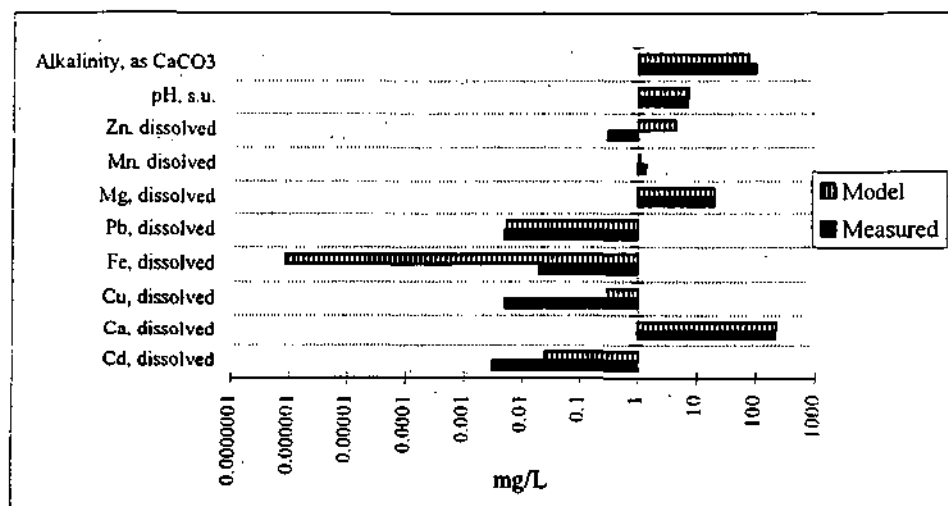


Figure 4.22b. Comparison of measured and modeled concentrations at CPDES Outfall 002, with liming at 600 lbs/day.

provided in the Appendix, and details the components and reactions used in the model. Basically, only 54 of approximately 150 possible components and 43 reactions were added. The reactions include equilibrium, complexation, and precipitation of the major metals of concern. Ions omitted from the model include sodium, potassium, chloride, whose concentrations do not appear to change significantly throughout the series of pond samples. The sulfate ion and all associated reactions, as apposed to the hydroxide and carbonate ions, seemed to be the only other practical component to remove from a carbonate system being treated with a hydroxide reagent. In addition, all bicarbonate complexes were omitted. The only solids allowed to precipitate were hydroxides and carbonates. According to the geochemical modeling a large percentage of many of the metals are bound in sulfate and bicarbonate complexes (Table 4.14). Therefore, omitting these reactions has resulted in an inaccurate modeling of the treatment plant and pond system.

The primary purpose of attempting to apply a process model to the adit drainage and lime treatment plant was to determine if the software available could accurately predict the conditions existing in this extremely complex solution. The mine drainage consists of a large variety of ions and solids in an electrolyte solution. Similar to the geochemical models available, process models must have all constituents and chemical reactions specified. In addition, thermodynamic and transport properties are required. It appears from these results and the inability of the model to function with all the necessary constituents and reactants, that the ASPEN Plus software is not applicable to modeling process involving extremely complex electrolyte systems such as the treatment of mine drainage.

## 4.7 Critique of the Current Plant and Conditions of the Ponds

The Rico Development Corporation currently operates and maintains a mine water treatment facility for the removal of heavy metals from the St. Louis adit discharge prior to its permitted discharge into the Dolores River. The drainage, with relatively high concentrations of metals and total dissolved solids (TDS), flows under natural conditions through a series of settling ponds following a lime neutralization treatment process.

The treatment process incorporates the slaking of approximately 600 lbs/day of calcium oxide (CaO) with a portion of the adit drainage diverted to the plant. The resulting lime slurry, at a pH of approximately 12, is then mixed with the remaining adit water as it flows directly into pond 18 where it has been assumed that adequate mixing in the pond would effectively treat all the drainage for the removal of permitted metals. Subsequent ponds are then used for facilitating gravitational sedimentation of the resulting solids prior to discharge at CPDES Outfall 002.

At the time of sampling (August, 1995), zinc and cadmium were out of compliance at the permitted discharge location. Physical observations of the site, as well as a brief explanation of the chemistry of the system may help explain the problem.

The general appearance of the St. Louis adit discharge changes from milky and orange tinted at the adit to relatively clear in the lower ponds. As was indicated in the analysis of samples taken from the adit and pond system, suspended metals were reduced by as much as 98% by the time the water reached the CPDES outfall. However, dissolved metal concentrations were elevated enough to cause total metal concentrations for zinc and cadmium to exceed permit limitations.

These results may indicate that the present rate of lime addition is not effective in reducing concentrations to permitted limits. The primary purpose of lime addition is to increase the pH of the water to a point where metal hydroxides will precipitate. The solubility of metal hydroxides is strongly dependent on pH, and a pH between 9 and 11 is

required in attaining a minimum solubility for the metals of concern in the drainage. A secondary mechanism for the removal of dissolved metals is their absorption onto existing solid particles and subsequent coprecipitation. Therefore, the addition of lime also increases the surface area available for this heterogeneous process. Since the pH in pond 18 is only 8.3, the first instinct would be to increase the amount of lime added. However, the physical characteristics of pond 18 indicate that the problem may be due to inadequate mixing rather than liming deficiencies. If the drainage is not completely mixed with the added lime, the necessary contact time needed for both reaction mechanisms will be reduced enough to prevent the proper removal of the constituents of concern.

A visual inspection of the ponds during the sampling activities in August of 1995 revealed that the uppermost ponds are almost completely full of solids. The volume estimates provided in Table 4.10 indicate that ponds 11 through 18 are 75% full of sludge. Moreover, ponds 18 and 15 are at 85% of capacity. This has caused the mine discharge to flow across the top of the sediment in sheets in addition to creating channelized flow patterns. Figure 4.23 shows the channels that have developed in pond 18. A second trip to the site in June of 1996, revealed that pond 15 is experiencing channeling as well.

A second consequence of the ponds filling with sludge is the reduction in the required residence time for facilitating gravitational sedimentation. Based on estimates displayed in Figure 4.20, the residence time of the drainage in the upper ponds has decreased by as much as 74% since the start of lime addition 12 years ago. This may result in higher suspended metal concentrations in the lower ponds due to solids spillover instead of sedimentation. These solids are then subject to more acidic conditions occurring in ponds 5 and 6 due to the geothermal springs located there, causing the suspended metals to re-dissolve and enter the Dolores River.

Conclusions from this analysis indicate that adding more lime to the system is not necessarily the solution to bringing all the metals into compliance and could actually compound the problem. The ponds, most notably 15 and 18, need to be dredged.
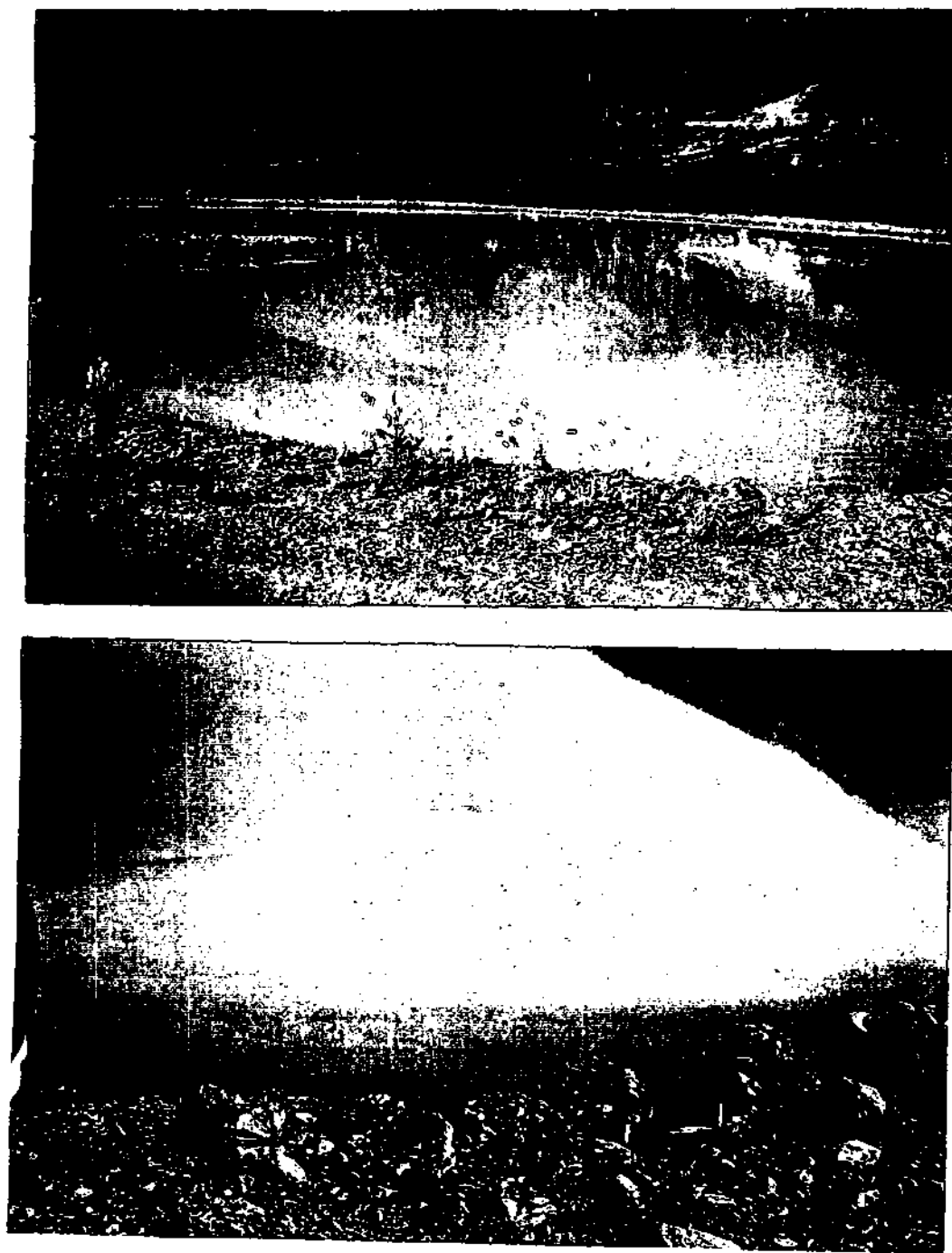
Figure 4.23. Channeling of the treated mine effluent in pond 18.

Without the removal of sludge, water quality at the CPDES outfall could worsen, and in as little as four years ponds 11 through 18 could be completely full of sludge.

The immediate concern, at this point, is bringing the adit discharge back into compliance with the CPDES permit limitations, and extending the lifetime of the ponds until a more suitable alternative treatment process can be established. Dredging, although not a permanent solution, could accomplish both of these goals for the short-term. In order to facilitate dredging operations in ponds 15 and 18, the water would have to be diverted to other ponds such as pond 13 or the new pond north of the site. Both of these ponds currently stand empty, and could effectively act as interim settling basins until dredging is completed.

Management of the dredged sludge poses another significant problem. Ponds 15 and 18 combined, represent approximately 8 tons (1.2 million cubic feet) of sludge with an average moisture content of 87%. Traditional approaches to managing this sludge include dewatering it to a moisture content of 50% to 60%, followed by disposal in off site land fills.

Dewatering is necessary for enhancing the handling characteristics of the sludge in addition to reducing the final volume to be disposed of. A thirty percent reduction in the moisture content of the sludge from ponds 15 and 18 would result in approximately 3 tons of sludge instead of 8 tons. This dewatering could be accomplished mechanically using centrifuges or pressure filters. However, previous dredging operations at the site found that simply storing the sludge in a dry holding pond successfully reduced the moisture content through evaporation.

Disposal of the dried sludge is dependent on the results of the Toxicity Characteristic Leaching Procedure (TCLP), as defined in the Federal Code of Regulations published by the EPA. This procedure is used for determining whether the sludge is hazardous or not, and has not been performed on dredged material at this site. However, the results could dictate whether disposal costs are as low as $28/ton for non-hazardous

waste, or as high as $220/ton for hazardous waste. These cost estimates do not include the cost of dredging, dewatering, or shipping to the landfills.

An alternative to disposal of the dried sludge is its use as a feedstock in smelting or cement operations. It has not been confirmed whether smelters or cement operations designed to handle such waste exists in the immediate area. However, this is definitely an option that needs to be pursued further since it could help off-set costs for remediation.

A conceptual approach to the volume reduction of sludge in the ponds, which could supplement dredging operations, would be to pump the extremely wet portion of the sludge back to the treatment plant for recycling. Assuming that the solids provide additional surface area for heterogeneous reactions, metal removal efficiencies could theoretically be maintained. Lime would continue to be added to maintain the required pH levels, but quite possibly at a reduced rate. The overall effect could be a reduction in the total amount of sludge produced. However, this is all obviously just speculation, and would have to be tested before considered for implementation.

## 4.8 Hypothetical Treatment Alternatives

Results from the discussion of the current treatment plant and conditions of the ponds clearly indicate that an immediate solution to the treatment of the St. Louis adit drainage needs to be established. Although many remediation technologies have been developed for the removal of metals from mine water, only those beyond basic research and /or specifically examined by other researchers for implementation at the St. Louis site have been mentioned here. In addition, these processes selected for further examination have demonstrated effective metals removal from other drainage with similar chemical and physical characteristics, and have the potential of long-term applicability.

The following discussion of process alternatives that may be considered applicable to the treatment of the St. Louis adit drainage is merely a conceptual approach to describing hypothetical solutions, and are largely derived from analysis performed by the Colorado School of Mines Research Institute (CSMRI 1982), Dr. Lorraine Filipek of Schafer & Associates (Filipek 1995), and Andre de Vegt of Paques, Inc. (de Vegt, et.al. 1993). It should be noted that these alternatives have not been tested in this study, and testing is beyond the scope of this thesis.

### 4.8.1 Lime Treatment with Sludge Recycle

Lime treatment with sludge recycle is commonly referred to as a high density sludge process (HDS), and was evaluated by CSMRI as an alternative treatment process for the St. Louis adit drainage in 1982. Figure 4.24 illustrates the process as it would apply to the adit drainage. Although this process is similar to what was proposed by CSMRI, some attributes of the site including the current treatment plant and the new pond have been incorporated into the design.

It has been proposed that the new pond could act as a holding pond to stabilize flow fluctuations and provide enough time for the iron hydroxide floc to settle prior to entering the lime treatment plant. However, given that the volume of this pond is only approximately 4.5 million gallons, the stabilization of seasonal variations is out of the question. The minimum volume required to stabilize seasonal variations was estimated to be 20 million gallons. However, this pond could be used to stabilize daily flow rates, providing an average retention time ($V_{pond}/Q_{adit}$) of four days. Here, $Q_{adit}$ is the monthly average flow rate from Table 4.12, multiplied by 1.4 to compensate for the consistent difference of 40% between the adit and outfall flow rates. Seasonal fluctuations could be compensated for by changing the influent to the plant as needed on a monthly basis.

Table 4.16 summarizes the advantages and disadvantages of lime treatment with sludge recycle (HDS process) as an alternative process for the treatment of the St. Louis adit drainage. The major advantage to this process is the technology has been proven to work for large flow rates such as those that occur at this site. In addition, the lime slaking portions of the treatment process and a holding pond for daily flow stabilization is already in place. However, this process does not guarantee non-hazardous sludge by products, and definitely requires pilot-scale testing to determine its feasibility.

Table 4.16: Advantages and disadvantages of the high density sludge process as an alternative process for the treatment of the St. Louis adit drainage.

| ADVANTAGES |
| --- |
| Lime treatment methods are established technologies. |
| HDS technology is well established. |
| HDS process has been proven to treat large flow volumes. |
| May provide long-term treatment capabilities / No sludge accumulation. |
| Possible reduction in the volume of sludge produced. |
| Produces drier sludges that may be applied as feedstock, offsetting treatment costs. |
| May provide a reduction in liming requirements. |
| The slaking reactor is already available. |
| The holding pond is already available. |
| Bench-scale tests for this specific drainage are complete. |

| DISADVANTAGES |
| --- |
| May require large capital expenditures for treatment equipment. |
| Could possibly incur higher operational and maintenance costs. |
| Produces sludge that may have to be disposed of. |
| The long-term commitment of continual treatment is discouraging. |
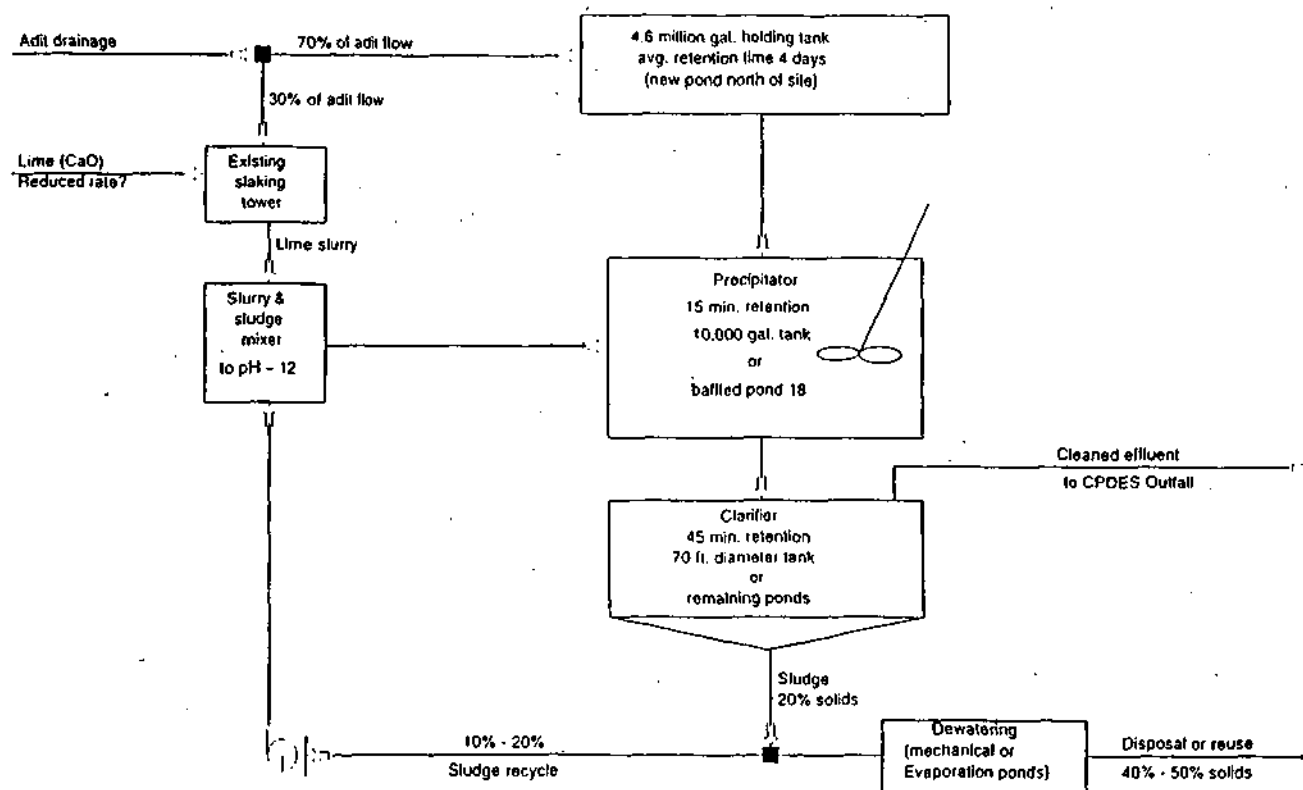
Figure 4.24: Hypothetical process flow diagram for the high density sludge process for treatment of the St. Louis adit drainage.

Since lime will continue to be added to maintain pH levels at about 12, the current lime slaking unit has also been incorporated into the design. As is currently being done, a portion of the adit drainage would be diverted to the slaking unit for creating the slurry mixture. This slurry would then be mixed with the recycled sludge prior to addition to the remaining adit drainage for neutralization and precipitation.

According to bench scale studies performed by CSMRI, 5 minutes was required to precipitate the metals, and 45 minutes was required to clarify the resulting mixture. Hence, based on a drainage rate of 2000 gpm the precipitator was estimated to be 10,000 gallons and the clarifier to be 70 feet in diameter (CSMRI 1982). Although the use of tanks for precipitation and a mechanical clarification would require considerable capital expenditures and possibly an increase in operation and maintenance costs, the removal of the spent sludge as it is produced could extend the life-time of the treatment process indefinitely since sludge storage would be eliminated. This process also renders the final sludge more amenable to reuse as feedstock for smelters or cement operations which could help off-set costs. Theoretically, by recycling 10% to 20% of the sludge produced, the final moisture content can be as low as 80% as compared to 95% to 98% moisture resulting from conventional lime treatment processes. The sludge would probably need further dewatering by mechanical means or evaporation in a dry pond, achieving 40 to 50% solids.

As an alternative to constructing tanks for precipitation and clarification, the ponds could be used, provided pond 18 was redesigned to contain baffles that would ensure adequate mixing in the precipitation process. In addition, the remainder of the ponds would have to accommodate a 45 minute residence time for proper clarification. However, this process depends upon sludge recycle from the treated effluent, and recycling from a settling pond could present material handling problems. Moreover, this could cause accumulation of sludge within the ponds which is desired to be avoided.

## 4.8.2 Biogenic H₂S Sulfide Precipitation

Biogenic $H_2S$ sulfide precipitation refers to the use of biologically produced hydrogen sulfide gas for the precipitation of dissolved metals in mine drainage. The $H_2S$ gas is generated by sulfate reducing bacteria which anaerobically oxidize organic material while reducing sulfate to $H_2S$. This process is particularly appealing because of the opportunity to use municipal sewage sludge as the organic substrate in the sulfate reduction process.

The town of Rico currently supports a population of about 100 people, the majority of which use on-site disposal systems such as septic tanks and tile fields for the treatment of their sewage. However, Rico is conveniently located 25 miles south of Telluride, and is in the path of growth as Telluride expands. While the septic tank and tile field is an acceptable form of sewage treatment for small populations, municipal waste water treatment systems become a necessity as populations increase. With this projected population growth of Rico in mind, a combined municipal waste water and mine drainage treatment system has been hypothesized.

Figure 4.25 illustrates the conceptual design of a biogenic $H_2S$ precipitation process for the treatment of the St. Louis adit drainage combined with municipal waste water treatment for the town of Rico. The design was developed by Andre de Vegt of Paques, Inc., after conversations with Dr. Filipek regarding the feasibility of this process for this site.

Preliminary calculations performed by de Vegt indicate that the sewage produced by a town of approximately 2000 people contains sufficient digestible organic matter to produce enough hydrogen sulfide gas to precipitate the metals of concern in the adit drainage. According to de Vegt, ethanol can be used to supplement the process if adequate sewage is not available.

**Municipal wastewater**
Pop: 2000
Flow: 140 gpm

Primary clarifier

Aeration basin

Secondary clarifier

Effluent

reduced sewage sludge

Municipal sludge

Flow: 0.7 gpm
TSS: 190 Kg/d
VSS 115 Kg/d

H2S gas

H2S gas

adit water & H2S gas

Solids Digester

Vapor/ liquid contactor

Precipitator & clarifier

Clean effluent
to CPDES Outfall

SO4 salt

Heat from geothermal springs

Adit drainage

Metal sulfide sludge

Figure 4.25: Conceptual design of a biogenic H$_2$S precipitation process for the treatment of the St. Louis adit drainage combined with municipal waste water treatment for the town of Rico.

Table 4.17 lists the assumptions used by de Vegt regarding the chemical qualities of primary sewage sludge for the conceptual design of the treatment plant. The estimate of the required population was based on the removal of 7 mg/L of zinc from an adit flow rate of 1100 gpm. According to de Vegt, approximately 100 gallons per day of municipal wastewater is produced per person. Hence, a population of 2000 would produce 140 gpm, on the average. Primary clarification of this wastewater would result in 0.7 gpm of primary sewage sludge containing 190 Kg/day of total suspended solids and 115 Kg/day of active biological mass used in the sulfate reduction process.

The solids removed from the primary clarifier are directed to a heated digester, where is it is assumed that water from the geothermal springs could be used for heating. In the digester, sulfate reducing bacteria use the biologically active fraction of the solids to reduce sulfate to hydrogen sulfide gas, assuming that 75% of the solids is available for sulfate reduction. According to de Vegt sulfate salts will probably have to be added to the solids digester to facilitate the oxidation-reduction reaction. The gas produced is then stripped from the digested sludge using inert nitrogen dioxide gas. Hypothetically, 75% of the $H_2S$ gas is stripped, and sent to a vapor-liquid contactor where the $H_2S$ in the vapor phase is transferred to the adit water. Once the $H_2S$ is in the liquid phase, it can react with the metals to form sulfide precipitates.

Spent sewage sludge is returned to the municipal wastewater treatment cycle for further treatment, and the adit water containing the $H_2S$ gas is sent to a precipitator and clarifier for metal sulfide removal. At no point in the cycle is the sewage sludge combined with the adit drainage. Hence, the sewage sludge contains no additional metals from the mine drainage and may possibly be used for composting and fertilization. The sulfide sludge produced from this process could hypothetically be sent to smelters for metal recovery, off-setting treatment costs. Depending on the desired sludge composition, one or more precipitation-clarification devices may be needed to selectively recover valuable metals.

Table 4.18 summarizes the advantages and disadvantages of the biogenic $H_2S$ sulfide precipitation process using primary sewage sludge from the town of Rico for the treatment of the St. Louis adit drainage. The major advantage of this hypothetical design is the beneficial applicability to both municipal wastewater and mine drainage treatment. In addition, metal recovery possibilities could off-set treatment costs. However, it is not certain whether the town of Rico will experience enough growth to provide the necessary sewage requirements for this process.

Table 4.17: Assumptions used for the conceptual design of the biogenic H₂S sulfide precipitation treatment plant using primary sewage sludge.

| Assumptions |
| --- |
| Municipal wastewater generated: 100 gal./day person |
| Primary sewage sludge produced: 0.0004 gal./day person |
| TSS[a] in sewage sludge: 50,000 mg/L |
| VSS[b] in sewage sludge: 30,000 mg/L |
| COD[c] in sewage sludge: 1 Kg COD/ Kg VSS |
| COD required for sulfate reduction: 1 Kg COD/ Kg SO₄²⁻ reduced |
| COD available for sulfate reduction: 75% |
| H₂S produced in solids digester: 1 mole H₂S produced / mole SO₄²⁻ reduced |
| Stripping efficiency of H₂S from digested solids: 75% |
| Zinc precipitated: 1 mole Zn²⁺ precipitates / mole H₂S produced |

[a] Total suspended solids.
[b] Volatile suspended solids. A measure of the active biological mass available.
[c] Chemical oxygen demand. A measure of the amount of organic matter available for oxidation.

Table 4.18: Advantages and disadvantages of the biogenic $H_2S$ sulfide precipitation process using primary sewage sludge from the town of Rico for the treatment of the St. Louis adit drainage.

| ADVANTAGES |
|---|
| Rico would receive a municipal wastewater treatment plant. |
| Obnoxious sewage gas utilized in mine drainage treatment. |
| Sewage sludge volume reduced through the oxidation-reduction process. |
| Ethanol could be used to supplement deficient sewage volumes. |
| Holding pond for stabilizing mine drainage flow to treatment plant already exists. |
| Metals removed in a more stable sulfide form. |
| Possible recovery of metal sulfides, off-setting treatment costs. |
| Effluents from each source kept separate. |

| DISADVANTAGES |
|---|
| May incur considerable capital costs for equipment. |
| Operational and maintenance costs would increase. |
| Produces a metal bearing sludge that may have to be disposed of. |
| Sewage from Rico would have to be pumped upstream to the treatment plant. |
| Town population is not currently large enough to support sewage requirements. |
| Would require bench-scale and pilot-scale testing to determine feasibility. |

### 4.8.3 Constructed Wetlands

Constructed wetlands are man-made passive treatment systems that mimic natural wetlands by employing the same geochemical concepts, while providing the opportunity to control and optimize the hydraulics and retention times within the system. This technology holds promise over the conventional lime neutralization process currently being used because large volumes of sludge are not generated, and long-term immobilization of metals could hypothetically be attained. However, management of the treatment system may include eventual removal and replacement of the contaminated substrate which could prove to be difficult, and may require costly disposal.

The use of constructed wetlands for treatment of the St. Louis adit drainage has been evaluated by Dr. Lorraine Filipek of Schafer & Associates (Filipek 1995). According to Dr. Filipek, the chemical attributes of the St. Louis adit drainage make it an ideal candidate for treatment with a series of passive treatment cells. However, large flow rates with extreme seasonal variations indicate the need for a combination of processes to accommodate high and low flow events and make it a less desirable option.

Figure 4.26 illustrates a conceptual process flow diagram for the treatment of the adit drainage with the estimated size requirements of the anaerobic cells determined by Dr. Filipek. Table 4.19 discloses the design criteria used to determine the sizing requirements based on metal loadings from the drainage, the necessary retention time within the system, and the permeability of the substrate proposed.

The conceptual design consists of a holding pond to help regulate flow into the system, a second pond to settle the iron hydroxide floc already present in the drainage, a series of anaerobic cells to precipitate other heavy metals as metal sulfides, and a final aerobic polishing pond. As discussed in section 4.5.2, a stabilization pond would be necessary to supply a constant flow to the reactors. However, the site is

Adit drainage

```
┌─────────────────────────────────┐
│   4.6 million gal. holding pond  │
│     residence time ~ 4 days      │
│      (new pond north of site)    │
└─────────────────────────────────┘

┌─────────────────────────────────┐
│  Iron hydroxide precipitation pond │
│        (pond 18 baffled)          │
└─────────────────────────────────┘

┌──────────────────────────────────────────┐
│        Vertical flow anaerobic cells       │
│          Total area 19.8 acres             │
│       substrate is composted manure        │
│             depth = 1 meter                │
│         Residence time = 3.5 days          │
└──────────────────────────────────────────┘

                 aeration
                 spillway

┌──────────────────────────────────────────────────────┐
│                  Aerobic wetland                        │
│            Total surface area = 15 acres                │
│                   depth = 1 meter                       │
│  Rock lined & colonized with green algae and cyanobacteria │
│               residence time = 5 days                   │
└──────────────────────────────────────────────────────┘
```

Clean effluent
CPDES Outfall

Figure 4.26: Conceptual process flow diagram for the passive treatment of the St. Louis adit drainage.

Table 4.19: Design criteria used for sizing the hypothetical wetland system.

| AEROBIC WETLAND CRITERIA |
| --- |
| Residence time, $\tau = 1.5$ days |
| Depth = variable, but usually very shallow (.5 - 1 foot) |
| Rock lined and colonized with green algae and cyanobacteria |

| ANAEROBIC WETLAND CRITERIA |
| --- |
| Residence time, $\tau = 3$ to 5 days |
| Depth = 3 feet |
| Vertical flow |
| Composted manure as substrate |
| Substrate permeability = 3 $(10^{-4})$ cm/s |
| Bacterial activity in new wetland = 300 mmol/m$^3$ day |
| Metal loading 20% of bacterial activity = 60 mmol/m$^3$ day |
| Sizing based on total zinc concentrations in the adit = 8 mg/L |
| Zinc loading rate = 4 g/m$^3$ day |

| FLOW RATE CRITERIA |
| --- |
| Average flow rate = 1.6 MGD |
| Maximum flow rate = 3.2 MGD |

not large enough to hold this pond and the other necessary treatment cells. Therefore, the new 4.7 million gallon pond north of the site, possibly in conjunction with pond 18. could be used as an initial settling pond. Pond 18 has been designated for use as a second settling pond. However, the flow through pond 18 is presently channelized (Figure 4.23) due to the large volume of sludge present. This pond could be made more efficient for iron precipitation by adding rock baffles and forcing the flow through the entire pond area. In addition, a majority of the sludge needs to be removed.

Based on the design criteria given in Table 4.19, the estimated surface area required for the aerobic wetland is approximately 7.5 acres for an average flow of 1.6 MGD, and 15 acres for a maximum flow of 3.2 MGD. This provides a residence time of 1.5 days in a pond averaging 1 foot deep. This pond should be of variable depth. and lined with rock that has been colonized with green algae and cyanobacteria to enhance manganese removal, and be preceded by an aeration spillway to ensure the water is highly oxidized (Filipek 1995).

The estimated surface area requirements for anaerobic cells is 9.4 acres for the average flow, and 19.8 for the maximum flow. This is based on vertical flow through three foot deep cells filled with composted manure, and provides the necessary residence time of 3.5 days.

The combined area requirements equate to approximately 35 acres not including the holding pond and pond 18. The total area available at the site, base on Figure 1.2, is about 30 acres. Hence, wetlands are not feasible to use as the sole treatment of the drainage. However, they could be used as a polishing step in conjunction with other treatment processes.

Table 4.20 summarizes the advantages and disadvantages of constructed wetlands for the use of treating the St. Louis adit drainage. The major advantage, of course, is the fact that wetlands are passive and would require minimal maintenance. However, the long-term applicability of wetlands has not been established. It is unknown whether the

metal loaded substrate will require removal and replacement, and in what period of time maximum metal capacities could occur.

Table 4.20: Advantages and disadvantages of constructed wetlands for use in treating the St. Louis adit drainage.

| ADVANTAGES |
| --- |
| Requires minimal operational and maintenance costs. |
| Could provide efficient metals removal. |
| Holding pond already exists, but not large enough. |
| Precipitation pond for iron hydroxide floc already exists. |

| DISADVANTAGES |
| --- |
| Could incur considerable capital costs. |
| May not have the necessary land requirements. |
| Lifetime of the substrate is uncertain. |
| Ultimate fate of metals removed from the drainage is uncertain. |
| Requires pilot-scale testing. |

Chapter 5

CONCLUSIONS

1. Flow rate measurements taken at the adit and at the CPDES Outfall indicate an overall loss of 40% of the drainage as it flows through the pond system. The adit flow rate at the time of measuring was 2200 ± 110 gpm, and the CPDES Outfall flow rate was 1400 ± 112 gpm. Possible causes for this loss were identified as an observed overflow of drainage from a hyplon-lined channel carrying water from the adit to the first pond, and possible seepage from pond 18. Material balance calculations performed at various locations within the pond system indicate that the channel overflow and seepage flow rates could be as high as 600 gpm, and 400 gpm, respectively.

2. A stabilization pond was considered for this site due to the large seasonal variation in flow rates. Estimates indicate that the minimum volume requirement for stabilizing the adit drainage would be approximately 20 million gallons (2.8 million cubic feet), with a uniform effluent flow of 1.09 million gallons per day (757 gpm). A stabilization pond would require approximately 95% of the total volume of ponds currently existing at the site.

3. Total recoverable, dissolved, and suspended cadmium, copper, zinc, lead, iron, and manganese in the adit and pond waters were measured to gain an understanding of the efficiency of the ponds as the water flows through the system. Results indicate that 70% to 95% of the total metals are removed from the pond system by the time the mine water leaves pond 11. Of the CPDES permitted metals, only cadmium and zinc were out of

compliance at the CPDES Outfall. Cadmium was measured to be 0.003 mg/L, and the 30-day average permit limitation is 0.0004 mg/L. Zinc was measured to be 0.3 mg/L, and the 30-day average permit limitation is 0.237 mg/L.

4. The analysis of the geothermal springs located near ponds 5 and 6 indicate extremely low concentrations of all the permitted metals (Cd, Cu, Pb, and Zn). However, dissolved concentrations of the same constituents in the pond 5 samples have increased while total concentration remained fairly constant. This is probably due to the fact that the spring water with a pH of about 6.5 is mixing with pond water with a pH of about 8, resulting in a lower pH at the outfall. Due to the amphoteric nature of metal hydroxides, a decrease in pH will cause the suspended material to redissolve.

5. After examining the results of the analysis of samples taken upstream and downstream from the apparent seep west of pond 18, seepage from the ponds cannot be confirmed. Since the entire area is geothermally active, it is entirely possible that the presence of the orange iron hydroxide precipitate in this channel occurs due to seepage from additional geothermal springs. Several constituents in the analysis tend to confirm the source as geothermal springs such as an increase in temperature, a decrease in pH, and no change in cadmium, copper, and lead concentrations. However, an increase in the other metals tends to support seepage from the ponds.

6. Core samples were taken from ponds 9, 11, and 18, and a grab sample was taken from the pond 5 sediment, where little or no sludge has been deposited. Pond 18 contained the deepest sludge, and this depth gradually became smaller throughout the pond system, confirming that most of the sedimentation is occurring in ponds 11 through 18. In addition, a visual inspection of each core, and the analysis of segments of each of the cores indicates homogeneity throughout the columns.

7. The sludge in ponds 9, 11, and 18 contain mostly calcium (30% on average) and iron (53% on average), relative to total concentrations in each core. However, manganese and zinc also have a strong presence, zinc at 10%, and manganese at 5%. In fact, it appears that manganese concentrations gradually increase in the sediment in the downstream direction. The concentrations of cadmium, copper, and lead are small relative to the other metals in all the ponds.

8. Analysis of the moisture content in the core samples indicates a compaction of the sludge with depth. Surface sediments contain only about 5% solids by weight, but the solids content increases exponentially to a maximum of approximately 25% solids. An emperical relationship between the fraction of solids and the average depth in centimeters is given by:

$$X_{solid} = 0.0562e^{0.0055(cm)}$$

9. Pond and sludge volumes were calculated for each pond in the system. The total empty pond volume was estimated to be 2,810,000 cubic feet. The total sludge volume was estimated to be 1,840,000 cubic feet. Most of the sludge resides in ponds 11 through 18, where it has been estimated that these ponds are 75% full of sludge. This has caused a 74% reduction in the residence time of the water in the upper ponds since liming began 12 years ago, from 15 days to 4 days. Furthermore, these sludge volumes have caused channelized flow patterns in ponds 15 and 18, and the consequence of this is an increase in metal concentrations downstream due to solids spillover instead of sedimentation.

10. Increasing the liming rate of the adit drainage is not necessarily the solution to bringing all the permitted metals into compliance with the CPDES permit requirements.

This could actually have the opposite effect by hastening the reduction of the needed residence time to settle out precipitated solids.

11. Dredging, although not a permanent solution, could bring the adit discharge back into compliance, and extend the lifetime of the ponds until a more appropriate and longer-term solution for treatment can be established. It has been recommended that both ponds 15 and 18 be dredged. To facilitate dredging operations, flow could be diverted to one or both of the empty ponds at the site (pond 13 and the new pond north of the adit).

12. The Toxicity Characteristic Leaching Procedure (TCLP) performed by PTI indicated that surficial sediments were not hazardous however, this test was not performed on the deeper pond sediments. Hence, it is not certain whether the entire depth of sludge is non-hazardous. Until this procedure can be performed on a more representative sample of the sludge, disposal requirements remain uncertain.

13. Lime treatment with sludge recycle has been proposed as a possible alternative treatment process for the St. Louis adit drainage. The major advantage to this process is that the technology has been proven to effectively remove metals from large flows such as those that occur at this site, while producing a reduced amount of sludge with a lower moisture content. In addition, the lime slaking portion of the treatment process and a holding pond for daily flow stabilization are already in place. However, this process does not guarantee non-hazardous sludge by products, and definitely requires pilot-scale testing to determine its feasibility.

14. A conceptual design of a biogenic $H_2S$ precipitation processes for the treatment of the St. Louis adit drainage combined with municipal waste water treatment for the town of Rico was developed. Preliminary calculations indicate that the sewage produced by a

town of approximately 2000 people contains sufficient digestible organic matter to produce enough hydrogen sulfide gas to precipitate the metals of concern in the adit drainage. The major advantage of this hypothetical process is the beneficial applicability to both municipal wastewater and mine drainage treatment. In addition, more stable metal sulfide sludges are produced, and metal recovery possibilities could off-set treatment costs. However, it is not certain whether the town of Rico will experience enough growth to provide the necessary sewage requirements for this process. Moreover, pilot-scale studies need to be performed at the site to determine the applicability of this process to the St. Louis adit drainage.

15. The use of constructed wetlands for treatment of the St. Louis adit drainage has been hypothesized as a possible treatment alternative. The conceptual design consists of a series of both aerobic and anaerobic cells. The combined surface area requirements equates to approximately 35 acres not including the holding pond and pond 18. The total area available at the site is about 30 acres. Hence, wetlands are probably not applicable. The major advantage of constructed wetlands is the fact that wetlands are passive and would require minimal maintenance. However, the long-term applicability of wetlands has not been established. It is likely that the metal loaded substrate will require removal and replacement, and it is unknown in what period of time maximum metal capacities could occur.

16. Results from the geochemical modeling using MINTEQA2 provided some insight into the nature of the adit drainage. For instance, the orange floc present in the drainage is probably iron and manganese hydroxides and manganese carbonate. Furthermore, most of the metals present in the dissolved state are either free ions, or hydroxide, carbonate, and sulfate complexes. Chloride and sodium didn't appear to play a significant role in the

overall chemistry of the drainage. This is consistent with the water quality data which indicated that chloride and sodium are relatively constant throughout the ponds.

17. Chemical engineering process modeling using ASPEN Plus was performed on the adit drainage and lime treatment plant to determine if this software could accurately predict the conditions existing in this extremely complex solution. The mine drainage consists of a large variety of ions and solids in an electrolyte solution. Similar to the geochemical models available, process models must have all constituents and chemical reactions specified. In addition, thermodynamic and transport properties are required. Results from the modeling attempt and the inability of the model to function with all the necessary constituents and reactants indicates that the ASPEN Plus software is not applicable to modeling processes involving extremely complex electrolyte systems such as the treatment of mine drainage.

Chapter 6

RECOMMENDATIONS

1. Investigate applicable technologies for dewatering the dredged sludge. Management of the dredged sludge poses a significant problem. Ponds 15 and 18 combined, represent approximately 8 tons (1.2 million cubic feet) of sludge with an average moisture content of 87%. Traditional approaches to managing this sludge include dewatering it to a moisture content of 50% to 60%, followed by disposal in off-site land fills. Dewatering is necessary for enhancing the handling characteristics of the sludge in addition to reducing the final volume to be disposed of. This dewatering could be accomplished mechanically using centrifuges or pressure filters, or by simply storing the sludge in a dry holding pond and reducing the moisture content through evaporation.

2. Perform TCLP extraction procedures on a representative sample of sludge from the ponds to be dredged. Disposal of the dried sludge is dependent on the results of the Toxicity Characteristic Leaching Procedure (TCLP), as defined in the Federal Code of Regulations published by the EPA. This procedure is used for determining whether the sludge is hazardous or not, and has not been performed on dredged material at this site. However, the results could dictate whether disposal costs are as low as $28/ton for non-hazardous waste, or as high as $220/ton for hazardous waste. These cost estimates do not include the cost of dredging, dewatering, or shipping to the landfills.

3. Investigate the recycling of some of the sludge in ponds 11 through 18 back through the lime treatment system as a way to reduce the overall volume. Assuming that the solids provide additional surface area for heterogeneous reactions, metal removal efficiencies could theoretically be maintained. Lime would continued to be added to maintain the required pH levels, but quite possibly at a reduced rate. The overall effect could be a reduction in the total amount of sludge produced. However, this is all obviously just speculation, and would have to be tested before considered for implementation.

4. Investigate the use of the dredged sludge as a feedstock in smelting and cement operations. It has not been confirmed whether smelters or cement operations designed to handle such waste exist in the immediate area. However, this is definitely an option that needs to be pursued further since it could help off-set costs for remediation.

5. Perform pilot-scale testing of the hypothetical processes presented to determine the applicability of each to the treatment of the St. Louis adit drainage.

6. Investigate the potential population growth of the town of Rico, and the need for municipal sewage treatment as a result of this growth.

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APPENDIX

<u>Input summary created by ASPEN PLUS Rel. 9.1-3</u>

UNITS: Metric
   Volume flow = $m^3/hr$
   Heat transfer coefficient =$Kcal/hr\ m^2\ K$
   Pressur = Bar
   Temperature = C
   Volume = $m^3$
   Molar density = $kmol/m^3$
   Mass density = $Kg/m^3$
   Molar enthalpy = $Kcal/mol$
   Mass enthalpy =.$Kcal/Kg$
   Molar concentration = mol/L
STREAM DEFINITIONS: All conventional
DATABANKS: Aspenpcd. Aqueous. Solids, Inorganic, Purecomp
PROP-SOURCES: Aspenpcd. Aqueous. Solids, Inorganic, Purecomp
COMPONENTS:
   $H_2O$, $H^+$, $OH-$, $HCO_3^-$, $CO_3-$, $Cd^{2+}$, $Ca^{2-}$, $Cu^{2+}$, $Fe^{3-}$, $Pb^{2+}$, $Mg^{2+}$, $Mn^{3+}$, $Zn^{2+}$,
   $Cu(OH)_2$, $Ca(OH)_2$, $CaCO_3$, $Cd(OH)_2$, $CdCO_3$, $Fe(OH)_3$, $Pb(OH)_2^*$, $PbCO_3$,     $Mg(OH)_2$, $MgCO_3$,
   $Mn(OH)_3^*$, $Mn_2(CO_3)_3$, $Zn(OH)_2$, $ZnCO_3$, $Pb(OH)_2(S)^*$, $Mn(OH)_3S^*$, $ZnCO_3S^*$, $Mn_2(CO_3)_3S^*$,
   $Cd(OH)_2S^*$, $Cu(OH)_2S^*$, $PbCO_3S^*$, $CdCO_3S^*$, $Pb(OH)_4^{+4}$, $Fe_2(OH)_2^{+4}$, $FeOH^{2+}$, $ZnOH^-$, $CaOH^-$,
   $MnOH^{2+}$, $MgOH^-$, $PbOH^-$, $Fe(OH)^{2+}$, $CO_2$, $CaCO_3(S)$, $Zn(OH)_2(S)$, $Fe(OH)_3(S)$, $Mg(OH)_2(S)$,
   $Ca(OH)_2(S)$, $MgCO_3(S)$, $Zn(OH)^{3-}$, $Pb(OH)_3^-$, $Zn(OH)_4^{-2}$
HENRY-COMPS: Global $CO_2$
CHEMISTRY GLOBAL :
. Dissociation reactions:
   DISS $MgCO_3 = Mg^{2+}\ 1 / CO_3^{2-}\ 1$
   DISS $Ca(OH)_2 = CaOH^-\ 1 / OH^-\ 1$
   DISS $Mg(OH)_2 = MgOH^-\ 1 / OH_-\ 1$
   DISS $Fe(OH)_3 = Fe(OH)_2^+\ 1 / OH^-\ 1$
   DISS $Zn(OH)_2 = ZnOH^-\ 1 / OH^-\ 1$
   DISS $CaCO_3 = Ca^{2+}\ 1 / CO_3^{2-}\ 1$
   DISS $Pb(OH)_2 = PbOH^-\ 1 / OH^-\ 1$
   DISS $Mn(OH)_3 = MnOH^-\ 1 / OH^-\ 2$
   DISS $Cd(OH)_2 = Cd^{2+}\ 1 / OH^-\ 2$
   DISS $CdCO_3\ Cd^{2+}\ 1 / CO_3^{2-}\ 1$
   DISS $Cu(OH)_2 = Cu^{2+}\ 1 / OH^-\ 2$
   DISS $PbCO_3 = Pb^{2+}\ 1 / CO_3^{2-}\ 1$
   DISS $Mn_2(CO_3)_3 = Mn^{3+}\ 2 / CO_3^{2-}\ 3$
   DISS $ZnCO_3 = Zn^{2+}\ 1 / CO_3^{2-}\ 1$
Equilibrium reactions:
   STOIC 1 $H_2O$ -1 / $H^+$ 1 / $OH^-$ 1
   STOIC 2 $CO_2$ -1 / $H_2O$ -1 / $H^+$ 1 / $HCO_3-$ 1
   STOIC 3 $HCO_3^-$ -1 / $H^+$ 1 / $CO_3^{2-}$ 1
   STOIC 4 $Fe^{3+}$ -1 / $H_2O$ -1 / $H^+$ 1 / $FeOH^{2+}$ 1
   STOIC 5 $FeOH^{2+}$ -1 / $H_2O$ -1 / $H^+$ 1 / $Fe(OH)_2^+$ 1
   STOIC 6 $Fe^{3+}$ -2 / $H_2O$ -2 / $H^+$ 2 / $Fe_2(OH)_2$ 1
   STOIC 7 $PbOH^-$ -1 / $OH^-$ 1 / $Pb^{2+}$ 1

STOIC 8 $Pb^{2+}$ -1 / $OH^-$ -3 / $Pb(OH)_3^-$ 1
STOIC 9 Pb+ -4 / $H_2O$ -4 / $H^+$ 4 / $Pb_4(OH)_4$ 1
STOIC 10 $MgOH^+$ -1 / $Mg^{2+}$ 1 / $OH^-$ 1
STOIC 11 $Mn^{3+}$ -1 / $H_2O$ -2 / $H^+$ 2 / $Mn(OH)_2^+$ 1
STOIC 12 $Zn^{2+}$ -1 / $OH^-$ -4 / $Zn(OH)_4^{2-}$ 1
STOIC 13 $Zn^{2+}$ -1 / $OH^-$ -3 / $Zn(OH)_3^-$ 1
STOIC 14 $CaOH^-$ -1 / $Ca^{2+}$ 1 / $OH^-$ 1
STOIC 15 $ZnOH^-$ -1 / $Zn^{2+}$ 1 / OH- 1
Associated equilibrium constants:
K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0
K-STOIC 2 A=231.465439 B=-12092.1 C=-36.7816 D=0
K-STOIC 3 A=216.050446 B=-12431.7 C=-35.4819 D=0
K-STOIC 4 A=-10.532563 B=0 C=0 D=0
K-STOIC 5 A=-14.585564 B=0 C=0 D=0
K-STOIC 6 A=-10.717564 B=0 C=0 D=0
K-STOIC 7 A=-21.976562 B=0 C=0 D=0
K-STOIC 8 A=44.055691 B=0 C=0 D=0
K-STOIC 9 A=-48.571564 B=0 C=0 D=0
K-STOIC 11 A=-28.400564 B=0 C=0 D=0
K-STOIC 12 A=50.950253 B=0 C=0 D=0
K-STOIC 13 A=25.263689 B=0 C=0 D=0
Precipitation reactions:
SALT $MgCO_3(S)$ $Mg^{2+}$ 1 / $CO_3^{2-}$ 1
SALT $Ca(OH)_2$ $CSOH^+$ 1 / $OH^-$ 1
SALT $Mg(OH)_2$ $MgOH^+$ 1 / $OH^-$ 1
SALT $Fe(OH)_3$ $FE(OH)_2^+$ 1 / $OH^-$ 1
SALT $Zn(OH)_2$ $ZnOH^-$ 1 / $OH^-$ 1
SALT $CaCO_3(S)$ $Ca^{2+}$ 1 / $CO_3^{2-}$ 1
SALT Cd(OH)2S $Cd^{2+}$ 1 / $OH^-$ 2
SALT $CdCO_3S$ $Cd^{2-}$ 1 / $CO_3^{2-}$ 1
SALT $Cu(OH)_2S$ $Cu^{2+}$ 1 / $OH^-$ 2
SALT $ZnCO_3S$ $Zn^{2+}$ 1 / $CO_3^{2-}$ 1
SALT $Pb(OH)_2S$ $PbOH^-$ 1 / $OH^-$ 1
SALT $PbCO_3S$ $Pb^{2+}$ 1 / $CO_3^{2-}$ 1
SALT Mn(OH)3S $Mn(OH)_2^+$ 1 / $OH^-$ 1
SALT $Mn_2(CO_3)_3S$ $Mn^{3+}$ 1 / $CO_3^{2-}$ 1
FLOWSHEET :
BLOCK SLAKER: Input = Lime  Output = Slurry
BLOCK REMIX: Input =Adit and Slurry  Output = CPDES
PROPERTIES: Ideal & Elecnrtl
Henry Componentents = GLOBAL
Chemistry = GLOBAL
True Components = YES
PROP-LIST:
PC / TC / OMEGA / MW / DHFORM / DGFORM / &
VLSTD / DGSFRM / DHSFRM :
PVAL "Pb(OH)_2" 50 / 2397 / .1 / 241.21 / -57.8 / &
-54.6 / 31.74 / -108.1 / -123.3

PVAL "Mn(OH)$_3$" 50 / 1938 / .1 / 88.95 / -57.8 / &
 -54.6 / 26.95 / -147 / -166.2
PVAL "Pb(OH)$_2$S" 50 / 2397 / .1 / 241.21 / -57.8 / &
 -54.6 / 31.74 / -108.1 / -123.3
PVAL "Mn(OH)$_3$S" 50 / 1938 / .1 / 88.95 / -57.8 / &
 -54.6 / 26.95 / -147 / -166.2
PVAL "Cd(OH)$_2$S" 50 / 2540 / .1 / 146.42 / -57.8 / &
 -54.6 / 30.57 / -113.2 / -134
PVAL "Cu(OH)$_2$S" 50 / 2360 / .1 / 97.56 / -57.8 / &
 -54.6 / 28.69 / -75 / -117
PVAL PbCO$_3$S 50 / 1954 / .1 / 267.21 / -57.8 / -54.6 &
 / 40.49 / -149.5 / -167.1
PVAL Mn$_2$(CO$_3$)$_3$S 50 / 2605 / .1 / 114.95 / -57.8 / -54.6 &
 / 37.08 / -195.2 / -213.7
PVAL CdCO$_3$S 50 / 1465 / .1 / 172.42 / -57.8 / -54.6 &
 / 40.1 / -160 / -179.4
PVAL ZnCO$_3$S 50 / 977 / .1 / 125.38 / -57.8 / -54.6 / &
 28.50 / -174.85 / -194.26
PROP-LIST DHFORM
PVAL Fe$^{3+}$ -57.8
PROP-DATA U-2
 PROP-LIST PLXANT
 PVAL "Pb(OH)$_2$" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL "Mn(OH)$_3$" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL "Pb(OH)$_2$S" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL "Mn(OH)$_3$S" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL "Cd(OH)$_2$S" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL "Cu(OH)$_2$S" 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
  1000.000
 PVAL PbCO$_3$S 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL Mn$_2$(CO$_3$)$_3$S 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL CdCO$_3$S 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL ZnCO$_3$S 7.97 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
PROP-DATA U-2
PROP-LIST CPSPO1
 PVAL "Pb(OH)$_2$" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL "Mn(OH)$_3$" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL "Pb(OH)$_2$S" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL "Mn(OH)$_3$S" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL "Cd(OH)$_2$S" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL "Cu(OH)$_2$S" 18.21 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL PbCO$_3$S 20.89 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
 PVAL Mn$_2$(CO$_3$)$_3$S 19.48 0.0 0.0 0.0 0.0 0.0 0.0 1000.000

```
      PVAL CdCO3S 18 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
    · PVAL ZnCO3S 19.05 0.0 0.0 0.0 0.0 0.0 0.0 1000.000
  PROP-DATA U-2
    PROP-LIST VSPOLY
    PVAL "PB(OH)2" 31.73 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL "Mn(OH)3" 26.65 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL "Pb(OH)2S" 31.73 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL "Mn(OH)3S" 26.95 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL "Cd(OH)2S" 30.57 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL "Cu(OH)2S" 28.69 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL PbCO3S 40.49 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL Mn2(CO3)3S 37.08 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL CDCO3S 40.10 0.0 0.0 0.0 0.0 0.0 1000.000
    PVAL ZNCO3S 28.50 0.0 0.0 0.0 0.0 0.0 1000.000
  PROP-DATA U-2
    PROP-LIST CPIG
    PVAL "Fe(OH)3(S)" 8400 0.0 0.0 0.0 0.0 0.0 0.0 1000.000  &
        1.0000E+28 1.0000E+28 1.0000E+28
    PVAL "Zn(OH)2(S)" 8400 0.0 0.0 0.0 0.0 0.0 0.0 1000.000  &
        1.0000E+28 1.0000E+28 1.0000E+28
    PVAL "CaCO3(S)" 8400 0.0 0.0 0.0 0.0 0.0 0.0 1000.000  &
        1.0000E+28 1.0000E+28 1.0000E+28
  PROP-DATA HENRY-1:
    PROP-LIST HENRY
    BPVAL CO2 H2O 159.1997 -8477.711 -21.95743 5.78075E-3  &
        -.1499939 226.8500
  PROP-DATA NRTL-1
    PROP-LIST NRTL
    BPVAL H2O CO2 10.06400 -3268.135 .2000000 0.0 0.0 0.0  &
        6.10352E-6 200.0000
    BPVAL CO2 H2O 10.06400 -3268.135 .2000000 0.0 0.0 0.0  &
        6.10352E-6 200.0000
  PROP-DATA GMELCC-1
    PROP-LIST GMELCC
    PPVAL H2O ( H+ OH- ) 8.045000
    PPVAL ( H+ OH- ) H2O -4.072000
    PPVAL H2O ( H+ HCO3- ) 8.045000
    PPVAL ( H+ HCO3- ) H2O -4.072000
    PPVAL H2O ( H+ CO3 2- ) 8.045000
    PPVAL ( H+ CO3 2- ) H2O -4.072000
PROP-SET MASSCONC MASSCONC SUBSTREAM=MIXED PHASE=L
PROP-SET PH PH SUBSTREAM=MIXED PHASE=L
PROP-SET SOLINDEX SOLINDEX SUBSTREAM=MIXED PHASE=L
STREAM ADIT DRAINAGE:
  Substream Mixed
  Temp=25, Pres=1.01325, Volume-Flow=493.92
```

Solvent=$H_2O$, Nphase=1, Phase=L, Tol=0.0001   Mass-Conc (g/L): $H_2O$ 1000 / $H^-$ 5.169E-7 / $OH^-$ 3.144E-7 /$HCO_3^-$ .09418 / $CO_3^{2-}$ .004e-3 $Cd^{2+}$ .025E-3 / $Ca^{2+}$ .21 / $Cu^{2+}$ .31E-3 / $Fe^{3+}$ .016 / $Pb^{2-}$ .018E-3 / $Mg^{2+}$ .02 / $Mn^{3+}$ 3.2e-3 / $Zn^{2+}$ 4.4e-3

STREAM LIME:
    Substream Mixed
    Temp=25, Pres=1.01325, Mass-Flow=100 <Lb/Day>
    Solvent=$H_2O$, Nphase=1, Phase=L
    Mass-Conc: $H^-$ 1.01E-14 / $OH^-$ 17 / $Ca^{2-}$ 20

BLOCK MIXER:
    Lime treatment plant

STREAM-REPORT:
    nomoleflow
    massflow
    ph
    mass concentration
    solubility index

Table A1: Initial scan of total metals in the adit and pond 5 samples. Concentrations are in mg/L.

| Constituent | Detection limits | Adit | Pond 5 |
|---|---|---|---|
| Aluminum | 0.05 | 1.8 | ND |
| Antimony | 0.05 | ND | ND |
| Arsenic | 0.0020 | 0.0029 | ND |
| Barium | 0.010 | 0.018 | 0.014 |
| Beryllium | 0.005 | ND | ND |
| Boron | 0.02 | ND | ND |
| Cadmium | 0.0001 | 0.025 | 0.003 |
| Calcium | 0.1 | 210 | 210 |
| Chromium | 0.01 | ND | ND |
| Cobalt | 0.01 | ND | ND |
| Copper | 0.005 | 0.31 | ND |
| Iron | 0.01 | 16 | 0.29 |
| Lead | 0.005 | 0.018 | ND |
| Magnesium | 0.1 | 19 | 20 |
| Manganese | 0.005 | 2.9 | 1.4 |
| Mercury | 0.0002 | ND | ND |
| Molybdenum | 0.010 | 0.031 | 0.024 |
| Nickel | 0.02 | ND | ND |
| Potassium | 1.0 | 1.5 | 2.0 |
| Selenium | 0.1 | ND | ND |
| Silicon | 0.5 | 6.8 | 5.3 |
| Silver | 0.0001 | ND | ND |
| Sodium | 3.0 | 7.1 | 8.4 |
| Strontium | 0.02 | 2.6 | 2.6 |
| Tin | 0.04 | ND | ND |
| Titanium | 0.02 | ND | ND |
| Vanadium | 0.01 | ND | ND |
| Zinc | 0.005 | 4.4 | 0.3 |

ND = not detected

Table A2: Water analysis of the adit and pond waters.

| PARAMETER | ADIT | POND 18 | POND 11 | | POND 9 | | POND 5 | |
|---|---|---|---|---|---|---|---|---|
| | SURFACE | SURFACE | SURFACE | INTERFACE | SURFACE | INTERFACE | SURFACE | INTERFACE |
| | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] | [mg/L] |
| Cadmium, Total | 0.025 | 0.0058 | 0.0038 | 0.0039 | 0.0038 | 0.0039 | 0.003 | 0.0035 |
| Cadmium, Dissolved | 0.022 | 0.0034 | 0.0028 | 0.0027 | 0.0029 | 0.0018 | 0.0031 | 0.0032 |
| Calcium, Total | 210 | 260 | 220 | 220 | 220 | 220 | 220 | 230 |
| Calcium, Dissolved | 210 | 220 | 200 | 210 | 210 | 210 | 210 | 220 |
| Copper, Total | 0.31 | 0.031 | 0.012 | 0.014 | 0.013 | 0.012 | < 0.005 | 0.006 |
| Copper, Dissolved | 0.007 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 |
| Iron, Total | 16 | 2 | 0.64 | 0.8 | 0.65 | 0.72 | 0.29 | 0.37 |
| Iron, Dissolved | 0.85 | 0.29 | 0.05 | 0.01 | 0.14 | 0.36 | 0.02 | 0.01 |
| Lead, Total | 0.018 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 |
| Lead, Dissolved | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 |
| Magnesium, Total | 20 | 19 | 20 | 20 | 20 | 19 | 20 | 21 |
| Magnesium, Dissolved | 19 | 18 | 18 | 18 | 18 | 18 | 20 | 20 |
| Manganese, Total | 3.2 | 1.7 | 1.8 | 1.7 | 1.7 | 1.8 | 1.4 | 1.5 |
| Manganese, Dissolved | 2.9 | 1.6 | 1.7 | 1.7 | 1.7 | 1.7 | 1.4 | 1.5 |
| Zinc, Total | 4.4 | 0.83 | 0.4 | 0.43 | 0.4 | 0.42 | 0.31 | 0.34 |
| Zinc, Dissolved | 4.3 | 0.21 | 0.2 | 0.19 | 0.24 | 0.19 | 0.3 | 0.32 |
| Potasium | 1.5 | 1.6 | 1.7 | 1.5 | 1.7 | 1.3 | 2 | 2.2 |
| Sodium | 7.1 | 8.3 | 8.1 | 8.3 | 8.2 | 8.3 | 8.4 | 9.2 |
| Sulfate | 420 | 350 | 530 | 550 | 310 | 310 | 570 | 510 |
| Chloride | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| DO | 6.2 | 6.3 | 6.9 | 4.4 | 7 | 4.9 | 7.9 | 6.5 |
| TSS | 42 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| TDS | 820 | 820 | 860 | 840 | 830 | 840 | 890 | 880 |
| Alkalinity as $CaCO_3$ | 77.2 | 70 | 68.8 | 66.8 | 67.6 | 66 | 98.4 | 90 |
| Bicarbonate as $HCO_3^-$ | 94 | 85 | 83 | 81 | 82 | 80 | 120 | 110 |
| Carbonate as $CO_3^{2-}$ | 0.004 | 0.416 | 0.259 | 0.246 | 0.285 | 0.153 | 0.022 | 0.021 |
| Total Carbonate as $CO_3^{2-}$ | 103 | 44 | 43 | 42 | 43 | 42 | 78 | 70 |
| Hardness as $CaCO_3$ | 608.3 | 720 | 570 | 600 | 633.3 | 629.2 | 633.3 | 630 |
| pH | 6.29 | 8.33 | 8.13 | 8.12 | 8.18 | 7.92 | 6.91 | 6.93 |
| Conductivity, uS/cm | 960 | 944 | 923 | 925 | 939 | 945 | 1039 | 1020 |
| Fe(II) | 1.5 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Temperature, C | 18.6 | 18.1 | 17.1 | 17.1 | 17.6 | 17.9 | 19.3 | 18.9 |
| Eh, millivolts* | 447 | 436 | 479 | | 503 | | 398 | |

*Eh values from June, 1995 ESA measurements
Results 5 times greater than detection limits have a 20% error due to dilution.

Table A3: Analysis of grab sample from pond 5.

| Constituent | Pore water, mg/L | Sediment, mg/Kg |
|---|---|---|
| Core length = grab sample | | |
| sample depth from top of core, cm | grab | grab |
| Cadmium, total | | 190 |
| Cadmium, dissolved | 0.0048 | |
| Calcium, total | | 18000 |
| Calcium, dissolved | 280 | |
| Copper, total | | 660 |
| Copper, dissolved | 0.005 | |
| Iron, total | | 100000 |
| Iron, dissolved | 0.1 | |
| Lead, total | | 300 |
| Lead, dissolved | 0.008 | |
| Magnesium, total | | 4400 |
| Magnesium, dissolved | 26 | |
| Manganese, total | | 66000 |
| Manganese, dissolved | 0.034 | |
| Zinc, total | | 18000 |
| Zinc, dissolved | 0.93 | |
| Potasium | 3.8 | 2600 |
| Sodium | 12 | <500 |
| Sulfide,mg/l | < 0.1 | |
| Sulfate, mg/l as $SO_4$ | 180 | |
| Chloride, mg/l | 3 | |
| DO, mg/l | 2.2 | |
| Alkalinity, mg/l as $CaCo_3$ | 282.5 | |
| Bicarbonate as $HCO_3^-$ | 338.7 | |
| Carbonate as $CO_3^{2-}$ | 0 | |
| Hardness, mg/l as $CACO_3$ | 810 | |
| pH, s.u. | 7.15 | |
| Conductivity, uS/cm | 1387 | |
| FE(II), ppm | < 0.1 | |
| Temperature, C | 23.2 | |

Table A4: Analysis of core samples from Pond 9.

| Constituent | | | | | | |
|---|---|---|---|---|---|---|
| Core length = 40 cm | Pore water,mg/L | | | Sediment, mg/Kg | | |
| Sample depth from top of core, cm | 0-5 | 10-20 | 24-40 | 0-5 | 10-20 | 24-40 |
| Cadium, total | | | | 180 | 100 | 86 |
| Cadmium, dissolved | 0.0068 | 0.0006 | 0.0007 | | | |
| Calcium, total | | | | 110000 | 75000 | 70000 |
| Calcium, dissolved | 260 | 250 | 250 | | | |
| Copper, total | | | | 1000 | 900 | 830 |
| Copper, dissolved | 0.005 | 0.005 | 0.005 | | | |
| Iron, total | | | | 110000 | 180000 | 180000 |
| Iron, dissolved | 0.06 | 0.08 | 0.08 | | | |
| Lead, total | | | | 240 | 450 | 500 |
| Lead, dissolved | 0.005 | 0.005 | 0.005 | | | |
| Magnesium, total | | | | 3600 | 2600 | 2800 |
| Magnesium, dissolved | 30 | 25 | 24 | | | |
| Manganese, total | | | | 34000 | 16000 | 11000 |
| Manganese, dissolved | 0.035 | 2.7 | 5.4 | | | |
| Zinc, total | | | | 31000 | 20000 | 17000 |
| Zinc, dissolved | 1.4 | 0.24 | 0.26 | | | |
| Potasium | 1.8 | 3.5 | 3.8 | 1600 | 1700 | 1700 |
| Sodium | 8.5 | 8.3 | 7.9 | <500 | <500 | <500 |
| Sulfide, mg/l | < 0.1 | < 0.1 | < 0.1 | | | |
| Chloride, mg/l | 3 | 3 | 3 | | | |
| DO, mg/l | 3.5 | 2.5 | 1.8 | | | |
| Alkalinity, mg/l as CaCo3 | 282.5 | 187.5 | 260 | | | |
| Bicarbonate as HCO3- | 338.7 | 224.8 | 311.8 | | | |
| Carbonate as CO32- | 0.0 | 0.0 | 0.0 | | | |
| Hardness, mg/l as CACO3 | 770 | 730 | 720 | | | |
| pH, s.u. | 7.24 | 7.61 | 7.55 | | | |
| Conductivity, uS/cm | 1326 | 1291 | 1291 | | | |
| FE(II), ppm | < 0.1 | < 0.1 | < 0.1 | | | |
| Temperature, C | 22 | 23.6 | 22.9 | | | |

Table A5: Analysis of Core samples from pond 11.

| Constituent | | | | | | |
|---|---|---|---|---|---|---|
| Core length = 160 cm | Pore water, mg/L | | | Sediment, mg/Kg | | |
| sample depth from top of core, cm | 0-24 | 100-110 | 155-160 | 0-24 | 100-110 | 155-160 |
| Cadmium, total | | | | 190 | 150 | 170 |
| Cadmium, dissolved | 0.0034 | 0.018 | 0.0056 | | | |
| Calcium, total | | | | 62000 | 15000 | 14000 |
| Calcium, dissolved | 250 | 260 | 220 | | | |
| Copper, total | | | | 1600 | 1800 | 2600 |
| Copper, dissolved | 0.032 | 0.005 | 0.005 | | | |
| Iron, total | | | | 180000 | 230000 | 200000 |
| Iron, dissolved | 0.01 | 0.01 | 0.01 | | | |
| Lead, total | | | | 400 | 770 | 1700 |
| Lead, dissolved | <0.005 | <0.005 | <0.005 | | | |
| Magnesium, total | | | | 5300 | 4400 | 2900 |
| Magnesium, dissolved | 26 | 29 | 27 | | | |
| Manganese, total | | | | 24000 | 8900 | 21000 |
| Manganese, dissolved | 0.005 | 0.005 | 0.005 | | | |
| Zinc, total | | | | 40000 | 36000 | 37000 |
| Zinc, dissolved | 0.96 | 3.4 | 1.5 | | | |
| Potasium | 1.5 | 1.7 | 1.4 | 2300 | 2300 | 1400 |
| Sodium | 9.2 | 8.5 | 8.5 | <500 | <500 | <500 |
| Sulfide, mg/l | <0.1 | <0.1 | <0.1 | | | |
| Chloride, mg/l | 3 | 3 | 3 | | | |
| DO, mg/l | 5.2 | 6.1 | 6 | | | |
| Alkalinity, mg/l as CaCo3 | 200 | 193.8 | 92.5 | | | |
| Bicarbonate as HCO3- | 239.8 | 232.4 | 110.9 | | | |
| Carbonate as CO32- | 0.0 | 0.0 | 0.0 | | | |
| Hardness, mg/l as CACO3 | 730 | 770 | 660 | | | |
| pH, s.u. | 6.97 | 6.92 | 7.47 | | | |
| Conductivity, uS/cm | 1287 | 1235 | 1148 | | | |
| FE(II), ppm | <0.1 | <0.1 | <0.1 | | | |
| Temperature, C | 25 | 19.9 | 19.6 | | | |

Table A6: Analysis of core sample from pond 18.

| Constituent | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Core length = 243 cm | Pore water | | | | Sediment | | | | | | | |
| sample depth from top of core, cm | 0-10 | 103-113 | 231-235 | 235-243 | 0-10 | 29-33 | 53-63 | 103-113 | 145-155 | 205-215 | 231-235 | 235-243 |
| Cadmium, total | | | | | 210 | 130 | 66 | 220 | 150 | 72 | 65 | 34 |
| Cadmium, dissolved | 0.0003 | 0.0008 | 0.0003 | 0.0014 | | | | | | | | |
| Calcium, total | | | | | 140000 | 140000 | 160000 | 130000 | 170000 | 250000 | 270000 | 39000 |
| Calcium, dissolved | 120 | 180 | 60 | 150 | | | | | | | | |
| Copper, total | | | | | 4100 | 1600 | 950 | 4300 | 910 | 730 | 400 | 540 |
| Copper, dissolved | 0.005 | 0.005 | 0.009 | 0.008 | | | | | | | | |
| Iron, total | | | | | 120000 | 72000 | 84000 | 160000 | 130000 | 68000 | 50000 | 260000 |
| Iron, dissolved | 0.02 | 0.42 | 0.02 | 0.01 | | | | | | | | |
| Lead, total | | | | | 170 | 100 | 100 | 370 | 130 | 100 | 140 | 1800 |
| Lead, dissolved | 0.005 | 0.005 | 0.018 | 0.011 | | | | | | | | |
| Magnesium, total | | | | | 22000 | 24000 | 15000 | 6800 | 7000 | 41000 | 16000 | 6000 |
| Magnesium, dissolved | 120 | 72 | 250 | 210 | | | | | | | | |
| Manganese, total | | | | | 13000 | 8300 | 7700 | 7500 | 8400 | 10000 | 12000 | 2800 |
| Manganese, dissolved | 0.005 | 0.13 | 0.018 | 0.057 | | | | | | | | |
| Zinc, total | | | | | 42000 | 26000 | 17000 | 54000 | 35000 | 16000 | 14000 | 6900 |
| Zinc, dissolved | 0.014 | 0.37 | 0.03 | 0.11 | | | | | | | | |
| Potasium | 1.5 | 1.9 | 5.2 | 2.8 | <500 | | | <500 | | | <500 | 3000 |
| Sodium | 9.1 | 11 | 8.7 | 9 | <500 | | | <500 | | | <500 | <500 |
| Sulfide, mg/l | 0 | 0 | 0 | 0 | | | | | | | | |
| Chloride, mg/l | 3 | 3 | 3 | 4 | | | | | | | | |
| DO, mg/l | 4.7 | 5.1 | 5.2 | 5.2 | | | | | | | | |
| Alkalinity, mg/l as CaCo$_3$ | 72.5 | 86.3 | 443.8 | 657.5 | | | | | | | | |
| Bicarbonate as HCO$_3^-$ | 86.9 | 103.5 | 532.1 | 788.4 | | | | | | | | |
| Carbonate as CO$_3^{2-}$ | 0 | 0 | 0 | 0 | | | | | | | | |
| Hardness, mg/l as CACO$_3$ | 790 | 740 | 1200 | 1200 | | | | | | | | |
| pH, s.u. | 7.6 | 7.4 | 7.62 | 8.19 | | | | | | | | |
| Conductivity, uS/cm | 1341 | 1363 | 2115 | 2293 | | | | | | | | |
| FE(II), ppm | 0 | 0 | 0 | 0 | | | | | | | | |
| Temperature, C | 20.6 | 25.6 | 26.9 | 34 | | | | | | | | |

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Table A7: Field analysis results of pore waters extracted from the cores from ponds 5, 9, and 11.

| Sample ID | Depth from top of core cm | Temperature C | pH s.u. | DO mg/L | Fe(II) ppm | Sulfide ppm | Conductivity uS/cm | Alkalinity mg/L as CaCO$_3$ |
|---|---|---|---|---|---|---|---|---|
| P5 PW2-01 | grab | 31.5 | 7.53 | 0.6 | nm | nm | 1380 | nm |
| P5 PW2-02 | grab | 23.2 | 7.15 | 2.2 | < 0.1 | < 0.1 | 1387 | 282.5 |
| P9 PW1-01 | 0-5 | 22 | 7.24 | 3.5 | < 0.1 | < 0.1 | 1326 | 282.5 |
| P9 PW1-02 | 5 | nm | 7.2 | nm | nm | nm | nm | nm |
| P9 PW2-01 | 5-10 | 23.3 | 7.45 | 2.9 | < 0.1 | < 0.1 | 1336 | 270 |
| P9 PW4-01 | 10-20 | 23.6 | 7.61 | 2.5 | < 0.1 | < 0.1 | 1291 | 187.5 |
| P9 PW5-01 | 20-24 | 22.3 | 7.34 | 2.2 | < 0.1 | < 0.1 | 1272 | 225 |
| P9 PW6-01 | 24-40 | 22.9 | 7.55 | 1.8 | < 0.1 | < 0.1 | 1291 | 260 |
| P11 PW1-01 | 0-24 | 25 | 6.97 | 5.2 | < 0.1 | < 0.1 | 1287 | 200 |
| P11 PW2-01 | 24-36 | 25 | 7.17 | 5.6 | < 0.1 | < 0.1 | 1185 | 160 |
| P11 PW3-01 | 36-46 | 25 | 7.02 | 5.3 | < 0.1 | < 0.1 | 1483 | 216.3 |
| P11 PW4-01 | 46-56 | 30.5 | 6.57 | 5.3 | < 0.1 | < 0.1 | 1570 | 272.5 |
| P11 PW5-01 | 56-66 | 26.7 | 6.56 | 5.3 | < 0.1 | < 0.1 | 1365 | 152.5 |
| P11 PW6-01 | 66-76 | 24.7 | 6.18 | 4.3 | < 0.1 | < 0.1 | 1236 | 121.3 |
| P11 PW7-01 | 76-86 | 25.8 | 6.94 | 5.1 | < 0.1 | < 0.1 | 1238 | 78.8 |
| P11 PW8-01 | 86-90.5 | 21.3 | 7.18 | 5.7 | < 0.1 | < 0.1 | 1381 | 243.8 |
| P11 PW9-01 | 90.5-100.5 | 22.5 | 7.17 | 5.1 | < 0.1 | < 0.1 | 1310 | 173.8 |
| P11 PW12-01 | 100.5-110.5 | 19.9 | 6.92 | 6.1 | < 0.1 | < 0.1 | 1235 | 193.8 |
| P11 PW13-01 | 110.5-112.5 | 21.3 | 6.89 | 5.9 | < 0.1 | < 0.1 | 1091 | 185 |
| P11 PW14-01 | 112.5-122.5 | 17.1 | 5.56 | 6.1 | < 0.1 | < 0.1 | 1070 | 100 |
| P11 PW15-01 | 122.5-132.5 | 23.7 | 7.14 | 5.2 | < 0.1 | < 0.1 | 1188 | 106.3 |
| P11 PW16-01 | 132.5-140 | 24.1 | 7.2 | 5.2 | 0.2 | < 0.1 | 1232 | 187.5 |
| P11 PW16-02 | 140-142.5 | 24 | 7.13 | nm | < 0.1 | < 0.1 | nm | nm |
| P11 PW17-01 | 142.5-147 | 23.2 | 6.57 | 4.3 | < 0.1 | < 0.1 | 1138 | 145 |
| P11 PW18-01 | 147-151.5 | 18.9 | 7.3 | 6.4 | < 0.1 | < 0.1 | 1099 | 161.3 |
| P11 PW19-01 | 151.5-155 | 19.4 | 7.24 | 5.8 | < 0.1 | < 0.1 | 1139 | 186.3 |
| P11 PW20-01 | 155-160 | 19.6 | 7.47 | 6 | < 0.1 | < 0.1 | 1148 | 92.5 |

Table A8: Field analysis results of pore waters extracted from the core from pond 18.

| Sample ID | Depth from top of core cm | Temperature C | pH s.u. | DO mg/L | Fe(II) ppm | Sulfide ppm | Conductivity uS/cm | Alkalinity mg/L as CaCO₃ |
|---|---|---|---|---|---|---|---|---|
| P18 PW1-01 | 0-10 | 20.6 | 7.6 | 4.7 | < 0.1 | < 0.1 | 1341 | 72.5 |
| P18 PW2-01 | 10-14 | 24.2 | 7.6 | 5.3 | < 0.1 | < 0.1 | 1596 | 136.3 |
| P18 PW3-01 | 14-18 | 28.3 | 7.83 | 5.6 | < 0.1 | < 0.1 | 2355 | 211.3 |
| P18 PW4-01 | 18-22 | 26.9 | 8.22 | 5.8 | < 0.1 | < 0.1 | 2713 | 722.5 |
| P18 PW5-01 | 22-25 | 27.2 | 8.34 | 5.6 | < 0.1 | < 0.1 | 2177 | 395 |
| P18 PW6-01 | 25-27 | 30.2 | 7.96 | 5.7 | < 0.1 | < 0.1 | 3954 | 1330 |
| P18 PW7-01 | 27-29 | 25.7 | 8.09 | 4.8 | < 0.1 | < 0.1 | 3386 | 1408.8 |
| P18 PW8-01 | 29-33 | 21.7 | 8.44 | 5 | < 0.1 | < 0.1 | 1877 | 288.8 |
| P18 PW9-01 | 33-43 | 22.2 | 7.41 | 4.7 | < 0.1 | < 0.1 | 1389 | 62.5 |
| P18 PW10-01 | 43-53 | 22.3 | 8.85 | 4.7 | < 0.1 | < 0.1 | 1396 | 101.3 |
| P18 PW11-01 | 53-63 | 33.3 | 7.85 | 5.1 | < 0.1 | < 0.1 | 1630 | 55 |
| P18 PW12-01 | 63-73 | 24.3 | 7.45 | 5.8 | < 0.1 | < 0.1 | 1316 | 41.3 |
| P18 PW13-01 | 73-83 | 22.3 | 7.42 | 5.3 | < 0.1 | < 0.1 | 1472 | 108.8 |
| P18 PW14-01 | 83-93 | 22.3 | 7.2 | 5 | < 0.1 | < 0.1 | 1355 | 103.8 |
| P18 PW15-01 | 93-103 | 32.5 | 7.34 | 5.1 | < 0.1 | < 0.1 | 1505 | 127.5 |
| P18 PW16-01 | 103-113 | 25.6 | 7.4 | 5.1 | < 0.1 | < 0.1 | 1363 | 86.3 |
| P18 PW17-01 | 113-123 | 26.6 | 7.32 | 4.6 | < 0.1 | < 0.1 | 1379 | 117.5 |
| P18 PW18-01 | 123-133 | 25 | 7.07 | 4.5 | < 0.1 | < 0.1 | 1428 | 133.8 |
| P18 PW19-01 | 133-135 | 32.4 | 6.89 | 5.3 | < 0.1 | < 0.1 | 1735 | 356.3 |
| P18 PW20-01 | 135-145 | 31.4 | 7.24 | 4 | < 0.1 | < 0.1 | 1677 | 212.5 |
| P18 PW21-01 | 145-155 | 33 | 7.24 | 3.7 | < 0.1 | < 0.1 | 1525 | 118.8 |
| P18 PW22-01 | 155-165 | 29.9 | 7.32 | 4.6 | < 0.1 | < 0.1 | 1614 | 151.3 |
| P18 PW23-01 | 165-175 | 25.7 | 7.41 | 4.4 | < 0.1 | < 0.1 | 1521 | 105 |
| P18 PW24-01 | 175-185 | 23.2 | 7.28 | 4.4 | < 0.1 | < 0.1 | 1331 | 171.3 |
| P18 PW25-01 | 185-195 | 28.2 | 7.37 | 4.3 | < 0.1 | < 0.1 | 1734 | 312.5 |
| P18 PW26-01 | 195-205 | 29.2 | 7.26 | 5.5 | < 0.1 | < 0.1 | 1598 | 48.8 |
| P18 PW27-01 | 205-215 | 30.1 | 7.9 | 4.7 | < 0.1 | < 0.1 | 1834 | 77.5 |
| P18 PW28-01 | 215-219 | 29.7 | 8.54 | 4.8 | < 0.1 | < 0.1 | 3066 | 427.5 |
| P18 PW29-01 | 219-223 | 32.7 | 8.28 | 3.7 | < 0.1 | < 0.1 | 2770 | 238.8 |
| P18 PW30-01 | 223-227 | 31.4 | 8.09 | 4.7 | < 0.1 | < 0.1 | 2366 | 222.5 |
| P18 PW31-01 | 227-231 | 30 | 8.13 | 4.8 | < 0.1 | < 0.1 | 2278 | 253.8 |
| P18 PW32-01 | 231-235 | 26.9 | 7.62 | 5.2 | nm | nm | 2115 | 443.8 |
| P18 PW33-01 | 235-242.5 | 34 | 8.19 | 5.2 | < 0.1 | < 0.1 | 2293 | 657.5 |

Table A9: Flow rates in MGD measured at the CPDES Outfall, 1984-1996.

| | 1984 | 1986 | 1989 | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1996* |
|---|---|---|---|---|---|---|---|---|---|---|
| January | 1.12 | 1.07 | 0.88 | 0.81 | 0.68 | 0.87 | 0.82 | 0.97 | 0.97 | 1.00 |
| February | 1.50 | 1.02 | 1.00 | 0.78 | 0.69 | 0.87 | 0.81 | 0.97 | 0.97 | 0.92 |
| March | 1.18 | 1.07 | 0.93 | 0.74 | 0.65 | 0.87 | 0.72 | 0.90 | 0.97 | 0.95 |
| April | 1.43 | 1.40 | 1.00 | 0.63 | 0.72 | 0.88 | 1.22 | 0.89 | 0.99 | 1.03 |
| May | 1.79 | 1.50 | 0.96 | 0.68 | 0.74 | 0.92 | 1.53 | 0.97 | 1.04 | 0.97 |
| June | 2.45 | 1.80 | 0.98 | 0.66 | 0.76 | 1.02 | 1.80 | 0.97 | 1.22 | 0.87 |
| July | 2.18 | 1.80 | 0.97 | 0.71 | 0.79 | 1.22 | 1.80 | 0.97 | 1.75 | |
| August | 1.86 | 1.60 | 0.93 | 0.70 | 0.81 | 0.92 | 1.48 | 0.97 | 1.72 | |
| September | 1.60 | 1.50 | 0.88 | 0.72 | 0.80 | 0.90 | 1.43 | 0.97 | 1.68 | |
| October | 1.40 | 1.40 | 0.86 | 0.74 | 0.75 | 0.81 | 1.23 | 0.97 | 1.68 | |
| November | 1.34 | 1.40 | 0.83 | 0.75 | 0.72 | 0.76 | 1.02 | 0.97 | 1.68 | |
| December | 1.17 | 1.28 | 0.82 | 0.68 | 0.87 | 0.87 | 0.97 | 0.97 | 1.42 | |

* Through 19 June, 1996

Table A10: Liming rates in lbs/day at the St. Louis treatment plant, 1984-1996.

| | 1984 | 1986 | 1989 | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1996* |
|---|---|---|---|---|---|---|---|---|---|---|
| January | 510 | 335 | 60 | 37 | 350 | 250 | 252 | 483 | 708 | 762 |
| February | 500 | 335 | 15 | 46 | 386 | 240 | 365 | 497 | 786 | 807 |
| March | 368 | 420 | 11 | 124 | 336 | 212 | 430 | 550 | 707 | 680 |
| April | 260 | 800 | 25 | 120 | 339 | 210 | 504 | 805 | 715 | 731 |
| May | 366 | 956 | 25 | 211 | 255 | 223 | 564 | 632 | 638 | 748 |
| June | 1036 | 1450 | 49 | 278 | 159 | 253 | 582 | 506 | 635 | |
| July | 916 | 1390 | 85 | 486 | 189 | 243 | 753 | 660 | 649 | |
| August | 1423 | 695 | 26 | 307 | 194 | 295 | 753 | 748 | 557 | |
| September | 904 | 570 | 12 | 211 | 174 | 284 | 693 | 694 | 504 | |
| October | 1209 | 370 | 15 | 199 | 175 | 277 | 58 | 627 | 627 | |
| November | 1216 | 300 | 14 | 290 | 254 | 503 | 290 | 755 | 699 | |
| December | 1690 | 300 | 10 | 352 | 254 | 140 | 227 | 740 | 775 | |

* Through 19 June, 1996